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AMBIENT TEMPERATURE BINDER CURE CATALYSTS
FOR HYDROXY TERMINATED SYSTEMS

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Final Technical Report
Contract FO 4611-70-C-0017

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Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
United States Air Force
Edwards, California 93523

aerojet solid propulsion company

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By

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FOREWORD

This technical report was prepared under Contract No. F04611-70-C-0017 as fulfillment of the requirements of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work reported was done in the Propellant Applications Section of the Aerojet Solid Propulsion Company, Sacramento, California. This report designated Aerojet Report 1486-01F, covers the results of work done during the interval 2 January 1970 to 31 July 1971. The program was monitored by Dr. J. Trout.

This report contains no classified information extracted from other classified documents.

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ABSTRACT

Catalyst systems which strike a satisfactory balance between potlife and time required for full cure have been developed for use in ambient cure catalysis of either R-45M or Li initiated HTPB propellants. The most sophisticated of these consists of the catalyst proper ($Fe(AA)_3$), a suppressor (HAA and/or α-hydroxy acid) which temporarily inactivates the catalyst, and a scavenger (ZnO) which slowly consumes the suppressor thus reactivating the catalyst. The other systems involve the use of a suppressor, either a chelating agent or an acid, to inhibit catalytic activity (the suppressor subsequently being consumed by reaction with propellant components) or the in situ formation of an active catalyst during cure. Aging, mechanical properties and processing are not adversely affected by these catalyst systems.

It is conclusively shown that the rate of cure will affect the final mechanical properties of the propellant, slower curing propellants being softer.

New information on the complexity of the propellant cure is presented, and new theoretical concepts, which have an important bearing on network analysis and interpretation of experimental data, have been advanced.

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GLOSSARY

u	Extension $(1 + \epsilon)$
acac	Acetylacetonate
AA	Acetylacetonate, used with metal symbol. Only a few are defined specifically in this glossary.
AP	Ammonium perchlorate
B-2000	Poly(1,2-butylene oxide) diol, M.W. 2000
BAAH	Benzoylacetylacetone
BuNCO	Butyl isocyanate
C-1	Bonding agent; N,N-di(2-cyanoethyl)-2,3-dihydroxypropylamine
Co-1	
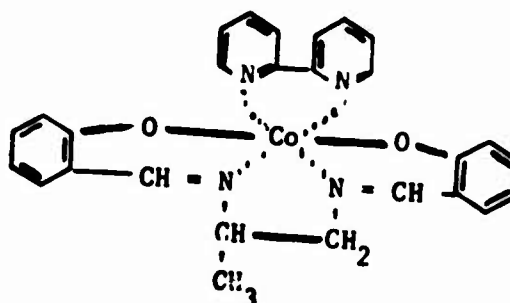
$Cr\ (HQ)_3$	Chromium 8-hydroxyquinolate
CTI	Cyclohexane triisocyanate
Cu-1	
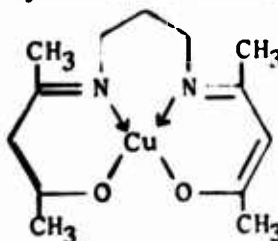
Cu-2	Same as Cu-1 with an N,N'-ethylene bridge
Cu-3	
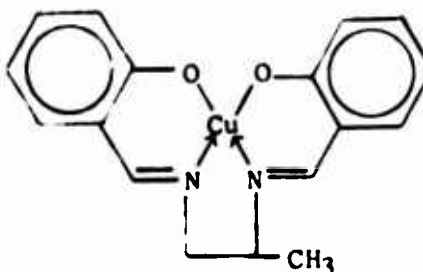
$Cu(AA)_2$	Copper acetylacetonate

GLOSSARY (Cont.)

D	Relative stress decay
d	Density or distance
DMP	Dimethyl phthalate
ds	Electron donor
DSC	Differential scanning calorimeter or calorimetry
ϵ	Elongation, $\Delta\ell/\ell$
$\dot{\epsilon}$	Strain rate
E	Equivalent weight or activation energy
E_o	Initial uniaxial, tensile modulus
en	Ethylenediamine
EW	Equivalent weight
f	Functionality
F_3AAH	1,1,1-Trifluoroacetylacetone
F_6AAH	1,1,1,5,5,5-hexafluoroacetylacetone
$Fe(AA)_3$	Ferric acetylacetonate
$Fe(DAc)_3$	Ferric dehydracetate
$Fe(F_3AA)_3$	Ferric 1,1,1-trifluoroacetylacetonate
$Fe(F_6AA)_3$	Ferric 1,1,1,5,5,5-hexfluoroacetylacetonate
$Fe(HQ)_3$	Ferric 8-hydroxyquinolate
$Fe(PhAA)_3$ or $Fe(\phi AA)_3$	Ferric 1-phenylbutandionate
$Fe(Ph_2AA)_3$ or $Fe(\phi_2AA)_3$	Ferric 1,3-diphenylpropanedionate
$Fe(TAM)_3$	Ferric 1,1-diacetylacetonate
GTRO	Glyceryl triricinoleate
HAA	Acetylacetone
HDAc	Dehydroacetic acid
HDI	Hexamethylene diisocyanate
HQ	8-Hydroxyquinoline
HTAM	Triacetylmethane
HTPB	Hydroxy terminated polybutadiene

GLOSSARY (Cont.)

IDP	Isodecyl pelargonate
ℓ	Length; subscripts o and s refer to initial and swollen lengths
LD-124	Poly(1,4-tetramethyleneoxy) diol, M.W. 1000
LHT-240	Poly(1,2-propylene oxide) triol, M.W. 720
Li HTPB	Lithium initiated, hydroxy terminated polybutadiene
μ	Flory-Huggins polymer-solvent interaction parameter
M	Molecular weight of chains between branch points, related to contour length of chain
M_c	Molecular weight of chains between branch points
MEK	Methyl ethyl ketone
$Mn(AA)_3$	Manganic acetylacetonate
$Mn(DAc)_3$	Manganic dehydracetate
$Mn(HQ)_3$	Manganic 8-hydroxyquinolate
$Mn(Ph_2AA)_3$ or $Mn(\phi_2AA)_3$	Manganic 1,3-diphenylpropandionate
MeOH	Methyl alcohol
MT-4	Bonding agent
MW	Molecular weight
ν_e	Moles of effective network
ν_o	Total moles of chains
ν_s	Moles of semiconnected chains
ν_t	Moles of terminated chains, a quantity denoting a negative crosslink density based on composition
ν_{th}	Theoretical crosslink density based on composition
ν'_{th}	Theoretical crosslink density (moles of branch points per gram of polymer) based on composition, $\nu'_{th} = 2\nu_{th}/3d$
Neozone D	Nominally N-phenyl-β-naphthylamine, an antioxidant
PAPI	Polyaryl polyisocyanate; PAPI-3 refers to the purified, trifunctional compound

GLOSSARY (Cont.)

PBD	Polybutadiene
PBNA	N-phenyl-β-naphthylamine (Neozone D)
PhAAH or ϕAAH	1-Phenyl-1,3-butanedione
Ph_2AAH or ϕ_2AAH	1,3-Diphenyl-1,3-propanedione
PhNCO	Phenyl isocyanate
PPG	Poly(propylene glycol), a hydroxy terminated polyether
ρ	Density
R-45M	Hydroxy terminated, free radical initiated polybutadiene
σ	Uniaxial tensile stress, subscripts m and b refer to maximum and at break
τ	Uniaxial retactive force
T-12	Dibutyltin dilaurate
TDI	Toluene diisocyanate
TEGDME	Tetraethylene glycol dimethyl ether
TEPAN	Bonding agent, Aerojet proprietary compound
$Th(AA)_4$	Thorium acetylacetonate
Thermolite T-12	Dibutyltin dilaurate
TP-340	Poly(1,2-propylene oxide) triol, M.W. 340
TP-440	Poly(1,2-propylene oxide) triol, M.W. 420
TP-2540	Poly(1,2-propylene oxide) triol, M.W. 2500
TP-4040	Poly(1,2-propylene oxide) triol, M.W. 4500
v_o	Volume fraction of rubber network in unswollen polymer
v_2	Gel fraction
$v_{2,p}$	Gel fraction of swollen plasticized polymer; $v_{2,u}$ refers to gel fraction of the above polymer if it were not plasticized
$v_{s,p}$	Volume fraction of semi-connected chains, plasticizer, or both

GLOSSARY (Cont.)

V	Volume, subscripts s and o refer to swollen and original (initial) volumes
V_1	Molar volume
W	Weight or weight fraction
$Zn(AA)_2$	Zinc acetylacetonate

AMBIENT TEMPERATURE BINDER CURE CATALYSTS
FOR HYDROXY TERMINATED SYSTEMS

I.   INTRODUCTION

This is the Final Technical Report submitted in fulfillment of the
requirements of Contract FO 4611-70-C-0017. This report covers the period
of 2 January 1970 to 31 July 1971.

Urethane propellants are normally cured at temperatures of 110-135°F.
A reduction of the cure temperature to 70-80°F would significantly reduce
propellant bore strains and bond stresses in case bonded solid rocket motors.
The lower cure temperature could also result in better propellant mechanical
behavior, because side reactions are also minimized at lower temperatures.
Ambient temperature curing is doubly important for propellants containing
energetic fuels for binder components, which may decompose during cure at
higher temperatures.

II.   OBJECTIVE

The objective of this program was the development of catalysts which
promote the isocyanate-hydroxy reaction at room temperature under the
conditions expected in a solid propellant environment and to demonstrate
the effectiveness of these catalysts. This objective had to be achieved
without seriously affecting propellant processing characteristics, mechanical
behavior and storage stability. Primary emphasis was on systems where the
casting and curing operations were within 5°F. While modified catalysts
were considered, principal emphasis was on commercially available catalysts.

III. SUMMARY AND RECOMMENDATIONS

A. A satisfactory balance between potlife and the time required for full cure is the major problem of ambient cure during which the accelerating effect of higher temperature on the urethane reaction cannot be utilized. This is particularly true for Li HTPB prepolymer cured with a diisocyanate both NCO groups of which possess equal reactivity, e.g., HDI.

At catalyst levels as low as 0.001% $Fe(AA)_3$ the propellant mix will be castable for only 30 minutes in case of HDI and somewhat longer for TDI cured propellants but still requires 7-10 days for full cure. In the absence of catalyst Li HTPB propellants are practically uncurable (weeks at 180°F are required). Reduction of the catalyst level below 0.001% entails the danger of losing the catalyst in degradative reactions. For these reasons some effort was spent searching for a catalyst of moderate activity which could be used in larger concentrations. Some of these were found, for example, ferric dehydro-acetate, but this approach was abandoned in favor of the more sophisticated catalyst systems described below.

B. Several highly satisfactory catalyst systems were developed to solve the problems encountered in the ambient curing of polyurethane binders and propellants. These systems are the catalyst-suppressor, the suppressor being either a diketone or an acid, catalyst-suppressor-scavenger, and in situ catalyst formation methods.

1. Catalyst-Suppressor System

A typical example is $Fe(AA)_3$-HAA. The HAA suppresses the catalytic acitivity of the $Fe(AA)_3$. This has the advantage that larger concentrations of the catalyst can be used, thus reducing the danger of losing the catalyst in degradative side reactions. In addition to $Fe(AA)_3$-HAA, practically all other iron chelate/chelating agent combinations can be used, except, perhaps, fluorinated acetylacetones and corresponding ferric complexes, because the latter slowly decompose into inactive FeF_3. A diketone may be used successfully with all metal complexes or salts. The simple catalyst-suppressor method has the advantage of greater simplicity over the catalyst-suppressor-scavenger method but requires longer times for full cure. A variant of this method is the substitution of an acid for the diketone scavenger.

2. Catalyst-Acid Method

This variation makes use of the equilibrium $M(AA)_3 + HX \rightleftharpoons$ $M(AA)_2X + HAA$, where M is a metal atom and HX a suitable acid. All acids which have a pKa of 6 or lower will liberate HAA from $Fe(AA)_3$ and thus increase potlife. The acids tested include acetic, chloroacetic, α-chloro-octanoic, α-bromotetradecanoic, linoleic, mandelic (phenylhydroxyacetic), benzilic (diphenylhydroxyacetic), lactic, phenylacetic, p-nitrophenylacetic and p-toluene-sulfonic acids. Of these, the best appear to be mandelic, benzilic, and p-nitrophenylacetic acids.

The advantage of acid over diketone is its greater reactivity with the scavengers or Al powder so that it is consumed faster than diketone to restore the activity of the catalyst and to shorten the required time for cure. A disadvantage is that acid is more reactive with isocyanate than diketone which can lead to softer propellants. This cure interference reaction is minimized by use of stronger acids which yield a more stable intermediate. The intermediate reacts with alcohol to form the urethane, e.g., $RNCO + HCl \rightarrow$ $RNHCOCl$; $RNHCOCl + ROH \rightarrow RNHCOOR + HCl$. This avoids chain termination. The weaker carboxylic acids form a mixed anhydride (carbamic acid-carboxylic acid anhydride) which decomposes to the corresponding amide, e.g., $RNHCO \cdot O \cdot COR \rightarrow$ $RNHCOR + CO_2$. Although less favored than the urethane reaction, it can and does occur causing some chain termination. Therefore, a good compromise appears to be a combination of HAA and acid to lessen chain termination without significantly decreasing the faster rate of cure.

The catalyst-acid method is also applicable to tin catalysts like the dibutyltin dilaurate (T-12) for which hitherto no modification of catalytic properties was available. T-12 might be of importance in some propellants where the danger of surface hardening is particularly high. Tin catalysts do not accelerate this undesirable reaction, but transition metal ions do.

3. Catalyst-Suppressor-Scavenger Method

Cure times can approximately be halved, if, in addition to the suppressor, a scavenger is used. The function of the scavenger is essentially to increase the rate of consumption of the suppressor, and by suitable choice of

the scavenger, to form an additional cure catalyst by reaction of the suppressor with the scavenger. The best scavenging compound that was found during this work was zinc oxide. This compound consumes both diketones and acids.

$$ZnO + 2HX \rightarrow ZnX_2 + H_2O$$

$$ZnO + 2HAA \rightarrow Zn(AA)_2 + H_2O$$
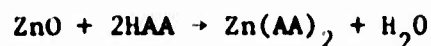
Either a soluble zinc salt or $Zr(AA)_2$ is a powerful catalyst. Lead monoxide is the next best choice but it combines only with the most acidic diketones and, of course, acids. Other basic compounds were found useful, e.g. a nickel tris-(ethylenediamine) complex, but were generally inferior to ZnO or PbO. The concentration of the scavenger was usually 0.1 weight %, based on the over-all propellant. However, its concentration is not critical and more or less may be used.

This cure system allows 8 to 12 hours of potlife and essentially cures Li HTPB propellant in 7 to 10 days at ambient. Full cure (no further change at room temperature) may take as long as 20 to 30 days.

Cure times are much shorter for R-45M propellants, which practically all catalyst systems will fully cure in 4 to 7 days with 8 to 12 hours potlife.

4. **In Situ Formation of Catalyst During Cure**

Zinc oxide and a diketone, but preferably an acid (e.g., linoleic, benzilic, p-toluenesulfonic acids) form an effective zinc catalyst during cure. This system was found very useful for R-45M/HDI propellants but practically useless for all other prepolymers including Li HTPB. The reason for this behavior is probably that the zinc catalyst is not specific for the urethane reaction. In R-45M propellants, owing to the large excess of hydroxyl groups over the NCO groups side reactions are minimized, but in stoichiometrically cured Li HTPB, side reactions become appreciable during the last stages of cure. This is essentially a consequence of a less favorable ratio of OH groups to impurities in the Li HTPB during the last stages of cure.

C.   The common feature of the methods worked out to overcome the problems mentioned above is a temporary delay of catalytic activity, to insure adequate potlife, followed by reactivation of the catalyst to ensure cure in a reasonable length of time. None of these methods have any deleterious effects on processing, aging and/or mechanical properties of the resulting propellant. On the contrary batch fluidity and thus, castability, are at a maximum because polymerization is delayed to a later stage, and the resulting mechanical properties are as good as any obtained by alternate methods. In addition, these methods are rather flexible, in that they allow catalyst activity to be modified at any stage of propellant processing. This is important in the case of certain bonding agents, e.g., C-1, alkanolamines, etc. which impart excessively high viscosities to the propellant batch until their hydroxyl groups are partially reacted. This can be achieved by first adding the catalyst only and after satisfactory batch fluidity is achieved, adding the suppressor.

D.   Ferric acetylacetonate was selected on the basis of performance and availability. Its performance is equaled by $Fe(\phi AA)_3$, $Fe(\phi_2 AA)_3$, $Fe(DAc)_3$, $Fe(AA)_2Cl$, $Fe(AA)_2ClO_4$, $Fe(AA)_2OCOCH(OH)\phi$ and $Fe(AA)_2O_3SC_6H_4CH_3$. The last four of these constitute new, hitherto unknown, compounds. The catalytic activity of practically all commercially available metal acetylacetonates and many metal soaps have been screened. In addition, other iron chelates of the promising metal cations, Fe^{3+} and Mn^{3+}, were synthesized. The screening tests (some of which were developed for this purpose) consisted of determinations of the (a) catalyst efficiency towards urethane catalysis, (b) catalyst ability to discriminate between aqueous and alcoholic hydroxyl groups, (c) catalyst effect on NCO homopolymerization and (d) catalyst stability in environment (hydrolysis).

Ferric and Mn^{3+} chelates showed high activity combined with highest ability to discriminate between water and alcohol. NCO homopolymerization also is not greatly affected by iron chelates. While ferric compounds are adequately stable, manganic chelates decompose very fast and were, therefore, not considered further. Dibutyltin catalysts, like dibutyltin dilaurate show less discrimination

between H_2O and ROH, thus, posing more problems for cure in environments with high moisture content. Thermal degradation of propellants subjected to high temperature is also more of a problem with alkyltin catalysts.

Stannous octoate and lead octoate and naphthenate were found to be good homopolymerization catalysts. Their hydrolytic stability is also rather poor.

Other important information gathered during this screening phase of the program was:

The effect of temperature on the uncatalyzed as well as the catalyzed ($Fe(AA)_3$, T-12) urea reaction with both HDI and TDI was ascertained and found to be significantly greater for HDI.

Most metal catalysts preferentially boost the urethane reaction. Uncatalyzed, the urea reaction actually is faster than the urethane reaction.

Homopolymerization of isocyanate is probably the second most important cause of cure failure. It is strongly accelerated by many metal catalysts. Particularly detrimental are divalent tin and lead compounds and copper derivatives.

Homopolymerization of phenyl isocyanate and butyl isocyanate indicate that trimerization of the isocyanate groups is the dominant reaction.

Investigation of a potential cure system using trimerization of excess NCO groups as a crosslinking reaction was terminated because of poor mechanical properties of the resulting propellants. Also a large variety of interference effects on homopolymerization, caused by minute changes of the environment, make this system unattractive.

Dry dissolved ammonium perchlorate slows the rate of the $Fe(AA)_3$ catalyzed PPG reaction, but otherwise appears not to affect the final extent of cure. Ammonium perchlorate inhibits timerization of TDI or HDI brought about by lead and tin catalysts, but not the trimerization of HDI catalyzed by copper compounds.

E.   Propellant reproducibility is linked to the rate of cure. It is
impossible to obtain the same mechanical properties for propellant with
different cure times whether because of lower level of catalysis, different
cure temperature, or both. The slower curing propellant will always be the
softer one (of course, only if no changes in composition of the two propellants
are made). The reasons for this are manifold. In the curing propellant several
reactions take place simultaneously. The three most important ones are urethane
formation, moisture-isocyanate reaction and isocyanate selfcondensation.
Depending on the bonding agents used, NH_3 formation, followed by immediate
reaction with RNCO, may also be significant. Of these only urethane formation
is desirable, and only it is significantly accelerated by a good cure catalyst.
Therefore, if the level of catalyst is lowered, the undesirable side reactions
will occur to a greater extent causing softer cure. The same effect is produced
by temperature changes, since the temperature coefficient of these reactions is
different. In addition, a new parameter, i.e. an effect of chain length distri-
bution on propellant properties, has been discovered. Since chain length
distribution is affected by changes of cure rate, the latter will affect
propellant reproducibility.

F.   It was conclusively shown that slow hardening of HTPB propellants
during high temperature aging is not associated with postcure, bonding agents,
etc., but is probably a consequence of the chemical nature of these prepolymers
(probably reactive double bonds). The effect is more pronounced in R-45M
propellants than Li HTPB.

G.   Discussions of new theoretical considerations, important
to propellant network analysis, have been included in this report.

H.   The following recommendations are made for future work.

1.   It is recommended that these catalyst systems be utilized in future, strategic and tactical missile systems.

2.   These catalyst systems should also be adapted to cures of propellants conducted above ambient temperature.

3.   Investigate the applicability and importance of chain length distribution on mechanical properties of hTPB propellants. Determine the magnitude of the effect of rate of cure on properties.

4.   Improve present techniques to analyze the network structure in present HTPB propellants. This would include both dynamic and equilibrium swelling measurements.

IV. TECHNICAL DISCUSSION

A. INTRODUCTION TO CATALYSIS

1. Uncatalyzed Urethane Reaction

It is well known that the backbone structure of binder prepolymers has a profound influence on their reactivity with isocyanates. For example in the absence of a cure catalyst, binder premixes of HDI and PPG type components can be stored for weeks without curing, while those of HDI and R-45M, a free radical initiated HTPB, cure in a matter of days. Similar effects can be produced by reacting simple alcohols in a variety of solvents. For example, in 0.15M solution, the reaction between 1-butanol and phenyl isocyanate proceeds about 500 times faster in heptane than in dioxane. Since the solvent plays such a large role, it is not surprising that changes of the concentration of the reactants have a more or less pronounced effect on the rate constant, depending on the type of solvent in which the reaction is run. Nevertheless, it is presently believed that the alcohol has a catalyzing effect on the rate of the urethane formation.[1] This alcohol catalysis goes back to the work of Baker,[2] who explained the concentration dependence of the rate constant by a mechanism in which isocyanate and a molecule of alcohol first form an activated complex which then reacts with a second alcohol molecule to form the product. The dependence of k_o, expressed as a second-order rate constant, on the alcohol concentration is given by Baker as

$$k_o = k_1 k_3 (ROH)/[k_2 + k_3(ROH)] \tag{1}$$

An analogous expression, in which the alcohol in the numerator is replaced by the base, has been given by Baker for base catalysis. It is derived from a similar mechanism according to which an intermediate base-isocyanate complex replaces the alcohol-isocyanate complex.

Obviously, k_o is not a true second-order constant, but
in spite of this, it has become conventional to report kinetic data in form
of second-order constants in the literature,[1] and most investigators obtained
their data from second-order plots.[2,5] Today, Baker's mechanism is probably
the most widely accepted one, although Ephraim, et al.[4] and notably Robertson
and Stutchbury[3] showed that the kinetic data obtained in solvents other than
dibutyl ether and benzene used by Baker were not compatible with the
above mechanism.

Oberth and Bruenner[6] showed that the rate of the uncatalyzed
urethane reaction depends essentially on the concentration of the polymeric
(self-associated) alcohol. Solvents, by breaking down the polymer, cause
a retardation of the reaction rate, the magnitude of which can be related
directly to the hydrogen bonding power of the solvent (Table 1). This
explains the strong dependency of the reactivity on the backbone structure
of the solvent. The high reactivity of the polymeric alcohol is attributed
to the polarization (weakening) of the OH bond in the polymer. The degree
of polarization, as indicated by the shift of the OH absorption band to
lower frequencies, is even more pronounced in amine-alcohol complexes, which,
accordingly, are strong catalysts for the urethane reaction. Infrared
studies have shown that the formation of the amine-alcohol complex and hence
the catalytic activity depends not only on the basicity of the amine but also
on steric factors. Dialkylanilines do not form hydrogen bonded alcohol-
amine complexes and do not catalyze the reaction, while pyridine, of approxi-
mately equal basicity, does form a complex and also accelerates the reaction.

Most investigators[2,5,7,8] who studied the urethane reaction in dilute
solution stated that it followed second order. It is easily seen that this
is so because, except for the most inert solvents (which have not been in-
vestigated previously), the alcohol exists practically entirely in the form
of the alcohol-solvent complex or in the monomeric form, depending on the
type of solvent used. We may write

TABLE 1

APPARENT SECOND-ORDER RATE CONSTANT FOR THE BUTANOL-PHENYL
ISOCYANATE REACTION IN VARIOUS SOLVENTS AT 25°C

Solvent	BuOH- PhNCO, M	$10^3 k_2$, M^{-1} min^{-1} Initial	at 50% Conversion
Cyclohexane	0.15	39	-
n-Heptane	0.15	39	-
	0.35	40	33
	0.80	44	28
Carbon tetrachloride	0.15	18	-
	0.80	39	28
m-Xylene	0.15	11	-
	0.80	26	19
Toluene	0.15	9.2	-
	0.80	25	22
Chlorobenzene	0.15	8.0	-
Benzene	0.15	5.8	-
	0.80	22	18
Chloroform	0.15	2.9	-
	0.80	18	16
1,2-Dichloroethane	0.15	2.7	-
	0.80	17.4	11
Dibutyl ether	0.15	2.1	-
	0.25	3.7	3.2
	0.50	6.5	4.7
	0.80	9.5	5.8
	1.00	11.5	6.5
	1.20	13.5	7.0
Nitrobenzene	0.15	1.8	-
Methyl ethyl ketone	0.15	0.33	-
	0.80	1.85	1.1

Increasing hydrogen bonding power of solvent.

TABLE 1 (cont.)

Solvent	BuOH-PhNCO, M	$10^3 k_2$, M^{-1} min^{-1}	
		Initial	at 50% Conversion
Butyl acetate	0.15	0.26	-
	0.80	2.5	2.0
Ethyl acetate	0.15	0.18	-
	0.80	2.4	1.6
Tetrahydrofuran	0.15	0.17	-
Acetonitrile	0.15	0.15	-
	0.80	1.3	1.25
Dioxane	0.15	0.08	-
	0.80	1.0	0.95
Diethylene glycol dimethyl ether	0.80	0.79	0.7ʋ

Increasing hydrogen bonding power of solvent.

$$\frac{du}{dt} = k_2 (ROH\text{-solvent})(RNCO) \tag{2}$$

The difficulty, however, arises when rate constants from reaction mixtures having different initial reactant concentrations are compared. Again, excepting the most inert solvents, it is found tha k_2 increases with the concentration of the reactants, particularly that of the alcohol. This increase of the rate constant is attributed to the appearance of the more reactive alcohol polymer, whose concentration will depend primarily on the concentration of the alcohol and the nature of the solvent. The high reactivity of the polymeric alcohol as well as the amine-alcohol complex can be explained by the polarization (weakening) of the OH bond of the alcohol molecule, which would facilitate the attack by the C atom of the isocyanate group. The activated complexes may perhaps be visualized as
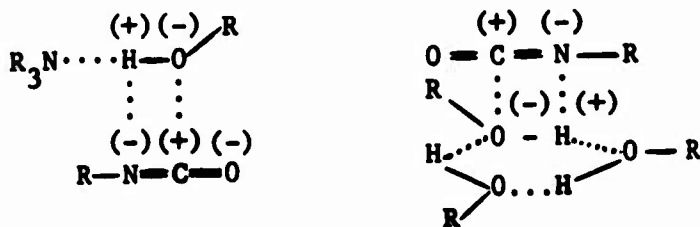
According to Badger and Bauer,[9] the polarization is directly related to the shift of the OH stretch band to lower frequencies. Thus the comparatively low reactivity of the monomeric alcohol, the alcohol-solvent complex, and the alcohol dimer would be due to the low degree of polarization of the OH bond, which is manifest from their spectra.

Assume that the reaction proceeds via the alcohol polymer-isocyanate intermediate, depicted above, whose rearrangement to the urethane

is the rate-determining step. This latter assumption is almost a necessity, because the equilibrium yielding the intermediate, like all the other hydrogen bonded alcohol-solvent complexes, is established instantaneously upon mixing. We may write

$$(ROH)_p + R^\frown NCO \rightleftharpoons complex \tag{3}$$

and

$$complex \rightarrow R^\frown NHCOOR + (ROH)_{p-1} \tag{4}$$
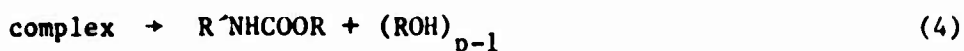
The rate of the uncatalyzed reaction is then given by

$$\frac{du}{dt} = k(complex) \tag{5}$$

This mechanism yields a kinetic expression (to conserve space the reader is referred to Reference 6 for details), which accounts reasonably well for the effects of solvents and/or concentration changes on the uncatalyzed urethane reaction.

2. Metal Catalysis

Metal catalysis particularly of aliphatic isocyanate-alcohol reactions can accelerate the reactions more than a million times, giving comparable speeds of cure for polyurethane employing either aromatic or aliphatic diisocyanates. In Table 2 some typical results are presented.[10]

The effect of solvents on the rate of urethane formation, is also largely overcome by metal catalysis (Table 3).

The activity of the catalyst decreases with increasing concentration, following a parabolic law. This nonlinearity has been explained[11]

TABLE 2

APPARENT SECOND-ORDER RATE CONSTANT FOR CATALYZED AND UNCATALYZED
REACTION OF 1-BUTANOL WITH BUTYL ISOCYANATE OR
PHENYL ISOCYANATE IN DIOXANE AT 25.5°C

Concentration of Reactants 0.65M
Catalyst ferric acetylacetonate, $Fe(AA)_3$

Isocyanate	$Fe(AA)_3 (10^3 M)$	k_2, $M^{-1} min^{-1}$
Butyl	-	$\sim 10^{-8}$
	2.6	0.32
Phenyl	-	0.85×10^{-4}
	2.6	0.16

TABLE 3

APPARENT SECOND-ORDER RATE CONSTANTS FOR CATALYZED AND UNCATALYZED
REACTION BETWEEN C_4H_9OH AND C_4H_9NCO BOTH 0.65M IN
VARIOUS SOLVENTS AT 25.5°C

Solvent	$Fe(AA)_3$, $10^3 M$	k_2, $M^{-1} Min^{-1}$
Benzene	2.62	0.54
	0.262	0.19
	-	2×10^{-4}
Dioxane	2.62	0.32
	0.262	0.09
	-	$\sim 10^{-8}$
Acetonitrile	2.62	0.16
	0.262	0.047
	-	$\sim 10^{-8}$
Methyl ethyl ketone	2.62	0.35
	0.262	0.12
	-	$\sim 10^{-7}$
Ethyl acetate	2.62	0.30
	0.262	0.08
	-	$\sim 10^{-8}$

by a mechanism in which the alcohol molecule is activated by the metal chelate through formation of an alkoxo acid:

$$2ROH + Fe(AA)_3 \rightleftharpoons [Fe(AA)_2OR)_2]H + HAA \tag{6}$$
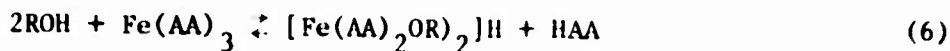
where HAA denotes acetylacetone. In a second step the alkoxo acid combines with the isocyanate to form an adduct whose rearrangement to the urethane is assumed to be rate determining--viz.,

$$[Fe(AA)_2(OR)_2]H + R'NCO \rightleftharpoons [Fe(AA)_2(OR)_2]H \cdot R'NCO \tag{7}$$

and

$$[Fe(AA)_2(OR)_2]H \cdot R'NCO \rightarrow R'NHCOOR + Fe(AA)_2OR \tag{8}$$
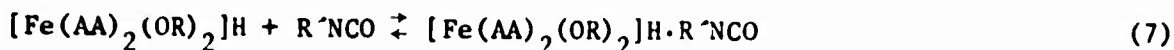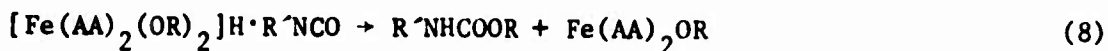
The $Fe(AA)_2OR$ is coordinatively unsaturated, and, therefore, adds another alcohol molecule and re-enters the cycle.

The above mechanism can be expressed mathematically by an equation of the form:

$$k_2 = k_o + A\{\sqrt{([HAA] + B)^2 + 4Bc} - ([HAA] + B)\} \tag{9}$$

where k_2 is the apparent second-order rate constant determined at a chosen point of conversion, k_o is the rate constant of the uncatalyzed reaction (negligible in the case of aliphatic isocyanates), and c is the catalyst concentration. HAA in Equation 9 is the quantity of acetylacetone added to the reaction mixture, and A and B are experimentally determined systems constants.

Equation 6 indicates that addition of HAA to the catalyst will suppress alcoholysis and thus will reduce its activity. This retardation

is hyperbolic with respect to HAA concentration as indicated by Equation 9 and is depicted in Figure 1. Addition of HAA to catalyzed systems was found to be a convenient way to modify the activity of cure catalysts and much use of it was made during this work.

B. CATALYST SCREENING STUDIES

A large number of commercially available catalysts were screened for potential use in this program. Several methods were employed.

1. Model Alcohol Studies

a. Reaction Exotherm Method

The effects of numerous catalysts on the reaction rate of the urethane reaction were evaluated by following the exotherm of HDI or TDI with methanol and 1-butanol. The exotherm method selected is particularly suited for screening purposes because it is fast, economical and very reproducible. The procedure used is as follows:

In a 150 ml beaker, 200 mg of the catalyst to be tested is added to 50 ml of the alcohol. Five milliliters of the diisocyanate are added with stirring and the temperature rise of the reaction is followed by a chromel-alumel thermocouple with an output of 4.1 mv/100°C. The signal is amplified and recorded on a strip chart recorder.

Since the heat exchange with the environment must be equal in all test runs, it is important that all reactions be carried out in the same apparatus and in the same manner. Thus, stirring rate and the size of the reaction vessel, as well as room temperature must be constant in all experiments. Under these conditions, faster reactions show a higher exotherm. Typical records for four of these reactions are shown in Figure 2.

The data from these tests have been reported in terms of an apparent second order rate constant, k_2. The values obtained are

DEPENDENCE OF THE REACTION RATE OF BUTANOL AND BUTYL ISOCYANATE
ON THE HAA-Fe(AA)$_3$ RATIO

(Benzene Solution, Fe(AA)$_3$ Concentration Constant)

Initial Concentrations: BuOH = 0.495 M

BuNCO = 0.867 M

Fe(AA)$_3$ = 2.62 x 10^{-3} M

k_2 x 10^3

HAA:Fe(AA)$_3$, mol ratio

Figure 1
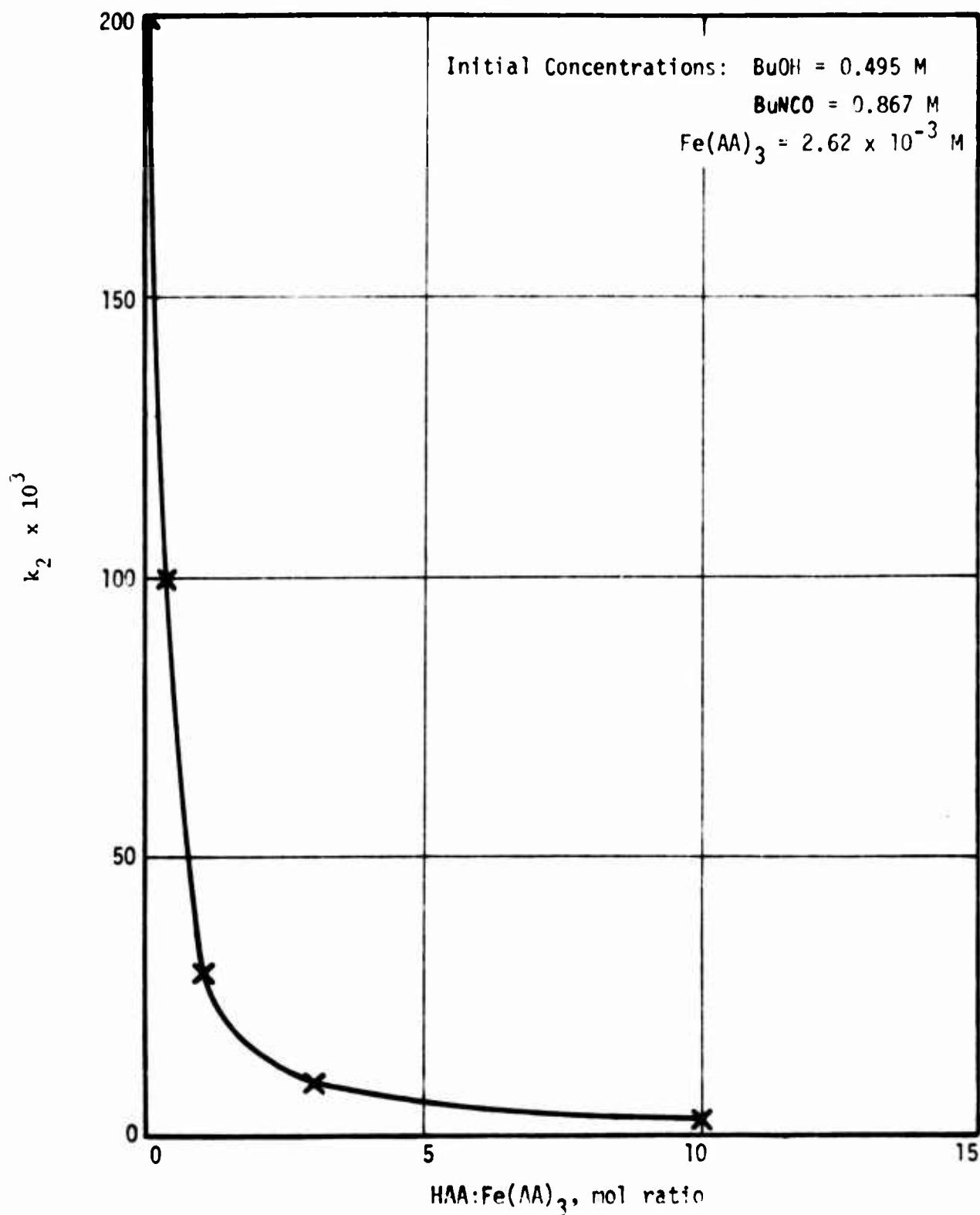
CATALYST SCREENING BY REACTION EXOTHERM

Time, Min. After Addition of Isocyanate

Figure 2
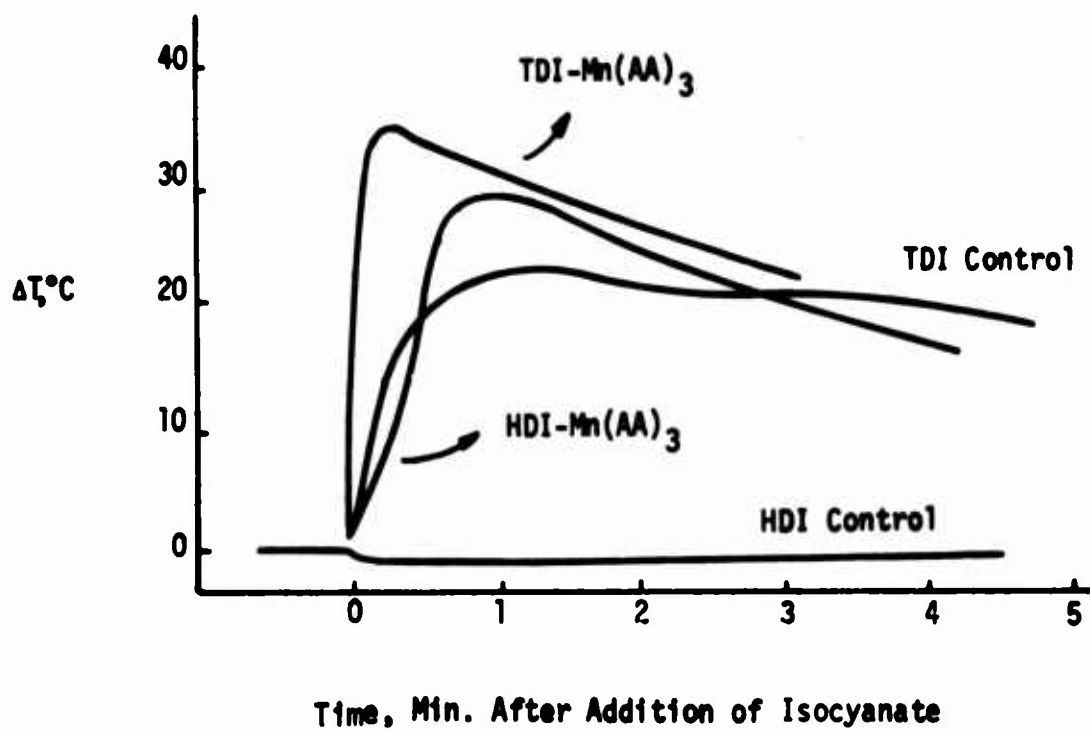
satisfactory for these screening tests. To report the data in this manner, it was necessary to calibrate the method by a known heat input. This was done by immersing a resistor in the reaction mixture and recording the heat rise of the total assembly due to the electrical energy input (watt-sec). For calibration, the apparatus was charged with the usual 50 ml of methanol and 5 ml of dimethyl phthalate (same heat capacity as HDI) to simulate the diisocyanate. With this mixture, an energy input at the rate of 48 watts yielded a temperature-time trace with an initial slope of $48°$. Based on the known heat of the urethane reaction (21,300 cal/mole) 48 watt min will have the same heat output as 3.24×10^{-2} equivalents of reacting alcohol and isocyanate. This number of equivalents in 55 ml solution corresponds to a rate of reaction of $0.589M \; min^{-1}$.

Only the initial slope of the exotherm is considered. At this point we may neglect heat losses. Then

$$k_2 = (dn/dt)/a_o \cdot i_o = 0.589/1.13 \times 22.6 = 2.3 \times 10^{-2} M^{-1} \; min^{-1},$$

i.e. the apparent second order constant of a reaction with an initial slope of $48°$ corresponds to $2.3 \times 10^{-2} M^{-1} \; min^{-1}$. The terms a_o and i_o are the concentrations of MeOH and HDI in moles per liter at the start of the reaction.

Because the initial concentrations are fixed as part of the procedure, the k_2 values for any catalyzed reaction will be proportional to the initial slope of the temperature-time curve. Thus
$k_2 = 2.3 \times 10^{-2} M^{-1} min^{-1} \cdot \tan \alpha / \tan 48°$, or simply $k_2 = 2.07 \times 10^{-2} M^{-1} min^{-1} \cdot \tan \alpha$, where $\tan \alpha$ is the slope of the exotherm. Similarly the factor for the butanol-HDI reaction was established.

The rate data for the catalysts screened by the exotherm method are listed in the approximate order of activity in the MeOH/HDI reaction in Table 4. In some cases the catalysts were incompletely soluble or gave a difficultly soluble precipitate in the alcohol.

TABLE 4

APPARENT SECOND ORDER RATE CONSTANTS OF CATALYZED ALCOHOL-ISOCYANATE REACTIONS BY THE EXOTHERM METHOD

(Cat. Conc. 0.2%, T ~35°C - Precision of Data $\pm$ 10%
Reactant Mixtures 50 ml ROH, 5 ml $R'(NCO)_2$)

Catalyst	$10^2 k_2 M^{-1} min^{-1}$		
	MeOH/HDI	MeOH/TDI	BuOH/TDI
$UO_2(AA)_2$	75[a]	28[a]	
$Zr(AA)_4$	22	22	
$In(AA)_3$	17[a]	38[a]	
$Cu(AA)_2$	16[a]	12[a]	
$Cu(Oct)_2$	16	15	
$Ni(AA)_2$	11[a]	16[a]	
$Ni(Oct)_2$	-	-	10
Zn Naph	9.0	22	16
Zn Decanoate	10[a]	28[a]	18
$Mn(AA)_3$	7.7	42	
$Bu_2Sn(Ac)$	6.6	28	
$Bu_2Sn(OCOC_{11}H_{23})_2$	5.1	25	
$Pb(AA)_2$	4.2[a]	38[a]	
$Cd(AA)_2$	3.8[a]	22[a]	
$Ce(AA)_4$	3.8[a]	22[a]	
$MoO_2(AA)_2$	3.6	11	
$Fe(AA)_3$	3.5	14	15
$Zn(AA)_2$	3.6	23	
$Ce(AA)_3$	3.2[a]		
Pb Naph	3.2	45	12
$Mn(AA)_2$	3.0[a]	20[a]	

a - Catalyst was either not completely soluble in reactant
mixture; or gave cloudy reaction mixture.

NOTE: Ac = CH_3CO; Oct = Octoate; Naph = Naphthenate ; Bu = Butyl

TABLE 4 (Cont.)

Catalyst	$10^2 k_2 M^{-1} min^{-1}$		
	MeOH/HDI	MeOH/TDI	BuOH/TDI
$Pb(Oct)_2$	2.1	26	12
$Co(AA)_3$	0.98	8.6	
$TiO(AA)_2$	-	8.6	
$Co(AA)_2$	0.87	11.	
$Sn(Oct)$	0.40[a]	13.[a]	10
$V(AA)_3$	0.21	10	
Cd Naph	0.19[a]	8.3[a]	
$(Bu_2SnO)_x$	0.19[a]		
$VO(AA)_3$	0.19	9.8	
$Ce(Oct)_4$	0.11[a]	7.4[a]	
$(Bu_2SnS)_3$	0.10[a]	15.[a]	
Bu_3SnAc	0.09		
Bu_3SnCl	0.08		
Control	<0.01	9.0	9.1

In general, those catalysts which were found to be the most effective with HDI were also the most effective with TDI. The tin catalysts are notable exceptions which cannot be explained at this time.

The effects of catalyst concentration were also studied in a few cases (Table 5 and Figure 3). It appears that at very low concentrations, the dependence of the rate constant on catalyst concentration deviates from the parabolic relationship which has been found at higher concentrations[10,11]. The behavior of Thermolite T-12 is especially peculiar in this respect (Figure 3). For the butanol-HDI reaction, the T-12 catalyzed reaction is slower than the FeAA catalyzed reaction at the lower catalyst concentrations, but faster than the FeAA catalyzed reaction at the higher concentrations. Since this is not observed for the butanol-TDI reaction, it is possible that the effect is due to an interaction between the T-12 and HDI.

The high activity noted for some of the catalysts tested in MeOH solutions (e.g. $UO_2(AA)_2$, $Pb(AA)_2$, etc) does not necessarily make them candidates for propellant use. There are two major factors, sensitivity to moisture and extremely low solubility in the commonly used binder systems, which may preclude their use in propellants. At present, it is not certain whether some of the cure failures which occur with catalysts like $UO(AA)_2$, $Th(AA)_4$, $Zr(AA)_4$, etc. are caused by catalyst degradation through moisture or catalyst induced side reactions.

b. Titrimetric Method

The second order rate constants for $Fe(AA)_3$ obtained by the exotherm method were compared with the rate constants by the titrimetric method. In the latter determinations, the urethane reaction (carried out under the same conditions as the exotherm method) was stopped by addition of dibutylamine, and the excess amine was back titrated with 1N HCl. A comparison of the data are shown in Table 6. Because of the rapid rate of

TABLE 5

APPARENT SECOND ORDER RATE CONSTANT OF CATALYZED MeOH/HDI REACTIONS

(Exotherm Method)

Catalyst	Quantity (mg)	Second Order Rate Constant 10^2 M^{-1} min^{-1}
$Fe(AA)_3$	1	0.05
	2	0.18
	5	0.59
	10	1.4
	20	2.1
	50	3.0
	100	4.5
	400	9.0
	1000	14.0
	2000	18

Catalyst	Quantity (mg)	Second Order Rate Constant 10^2 M^{-1} min^{-1}
$UO_2(AA)_2$	5	6.8
$UO_2(AA)_2$	20	17
$UO_2(AA)_2$	100	57
$Zr(AA)_4$	20	3.2
$Zr(AA)_4$	100	11
$In(AA)_3$	10	1.1
$Th(AA)_4$	10	0.96
$Mn(AA)_3$	10	0.82
$Cu(AA)_2$	10	1.3

EFFECT OF CATALYST LEVEL ON THE RATE OF THE
BuOH-TDI AND BuOH-HDI REACTION

(Exotherm Method)

Figure 3
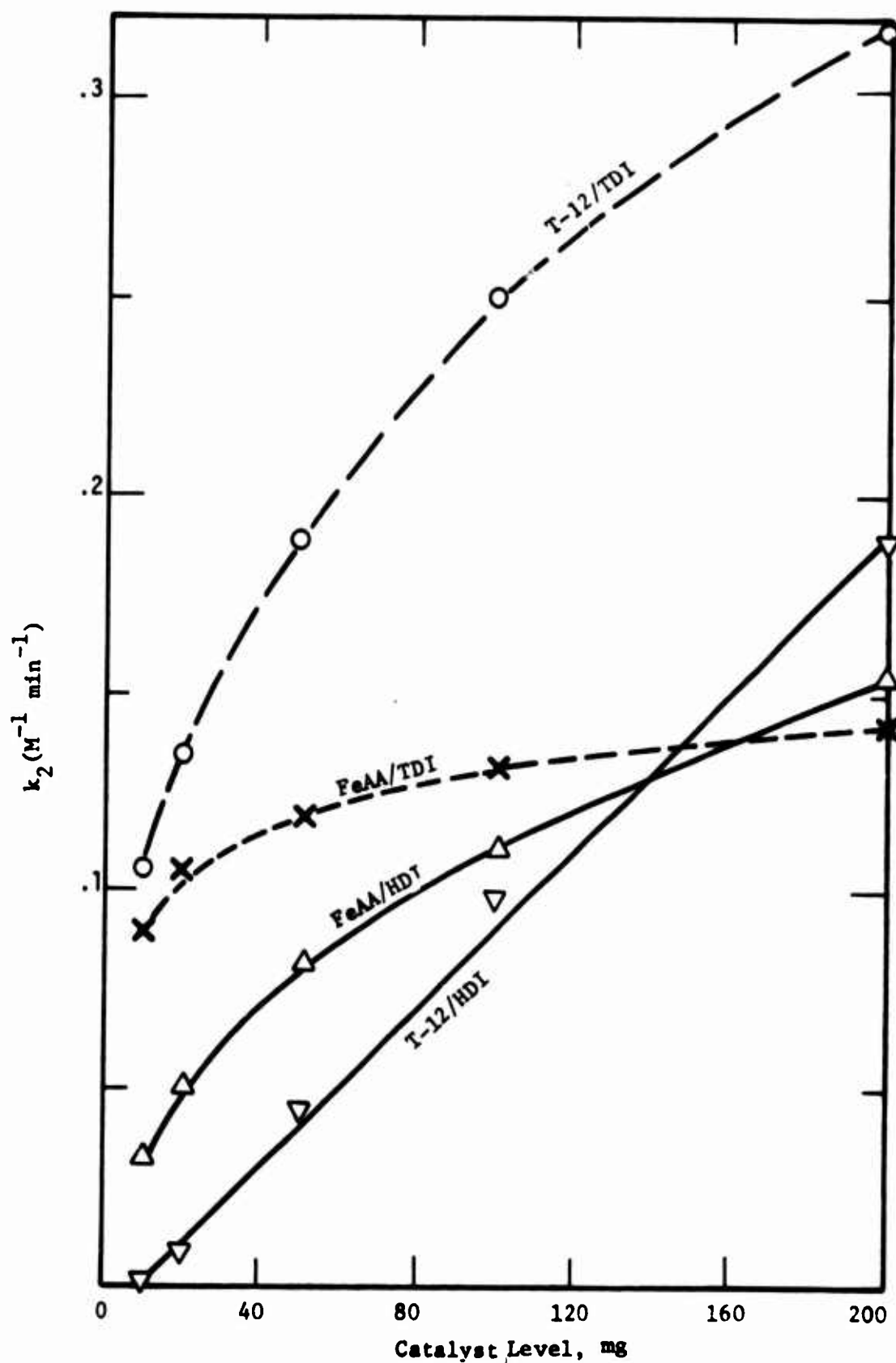
the reaction at these high reactant concentrations, only low catalyst con-
centrations could be evaluated titrimetically, where the times required to
start and stop the reaction are small compared to the total time of reaction.

TABLE 6

COMPARISON OF k_2 VALUES FROM TITRIMETRIC AND EXOTHERM
METHOD. 50 ml METHANOL AND 5 ml HDI CATALYZED WITH Fe(AA)$_3$

Fe(AA)$_3$, mg	$10^2 k_2$ (Exotherm)	$10^2 k_2$ (Titrimetric)
1	0.05	0.04
2	0.18	0.21

The agreement shown between the two methods is considered satisfactory for
this phase of the program.

2. **Binder Simulants**

    More meaningful rate data are obtained if the catalyst is
tested in a binder system which closely approximates the one used in actual
propellants. Two representative prepolymers were selected for these tests:
R-45, an HTPB with primary functional groups, and PPG, a polypropylene
oxide diol. Both were diluted with IDP (isodecyl pelargonate) plasticizer
so that the final composition of the two systems was respectively:

PPG System

IDP	35%	IDP	35%
Butyl isocyanate	9.9%	Butyl isocyanate	8.4%
PPG	54.7%	R-45	56.4%
Catalyst	0.4%	Catalyst	0.2%

Both mixtures closely resemble actual propellant binders with the exception
of using the monoisocyanate in place of a di- or triisocyanate. The

monoisocyanate is important to keep the mixture fluid and analytically
tractable. The method used for the determination of rate constants consists
of adding the isocyanate (2 ml) to a stoichiometric quantity of the hydroxyl
compound/IDP mixture (approx. 20 ml) contained in a 500-ml Erlenmeyer flask.
The isocyanate was thoroughly mixed into solution with a magnetic stirrer
and the mixture was then allowed to react for a given length of time at 25°C
in a water bath controlled to ±0.1°C. The reason for the large Erlenmeyer
flask is to spread the reaction mixture over a large area facilitating heat
exchange for temperature control. The reaction was again stopped by addition
of excess dibutylamine, which was back titrated with 1N aqueous HCl. A
suitable indicator for titration is a mixture (3:1) of bromocresol green and
methyl red (appr. 0.1% in MeOH). Prior to titration the reaction mixture was
diluted with methanol in order to make it compatible with the aqueous HCl.
The HTPB system was diluted in addition with approximately 50 ml benzene,
prior to dilution with methanol. A finely dispersed emulsion results which
can be titrated, otherwise the HTPB remains as a tough coherent layer on the
bottom of the flask. Since the catalyzed, as well as the uncatalyzed, urethane
reaction is not really second order, the average of several determinations
(usually 3 points) which were spaced at approximately 25%, 50% and 75%
reaction is reported. All of the catalysts tested markedly increase the
rate of reaction (Table 7). If only the activity of the catalysts were
important, most of the catalysts could be used for propellant binders, since
differences of activity can be largely compensated by changes in concentration.
However, individual catalysts have shown marked differences in gumstock cure
tests and even greater differences have been observed in propellant cure
tests. These tests are discussed below.

3.   Binder Cure Studies

        The more promising catalysts found in the reaction rate
studies were further tested in two binder systems. These binders are based
on R-45/IDP/HDI and PPG/TP-4040/IDP/HDI. In both cases, the IDP concentration

TABLE 7

APPARENT SECOND ORDER RATE CONSTANTS FOR THE R-45/IDP/BUTYL ISOCYANATE (0.5M) AND THE PPG/IDP/BUTYL ISOCYANATE (0.63M) REACTION AT 25°C[a]

Catalyst	$10^2 k_2$ (M^{-1} min^{-1})	
	HTPB (R-45)	Polyether (PPG)
$Fe(AA)_3$	1.7	2.1
$Mn(AA)_3$	2.3	2.4
$Cu(AA)_2$	0.55[b]	1.6[b]
$Zn(AA)_2$	1.7[b]	2.0
$Bu_2Sn(OOCC_{11}H_{23})_2$	1.8	1.4
$Bu_2Sn(OOCCH_3)_2$	1.4	1.7
$(Bu_2SnS)_3$	1.5	1.5
$Sn(OOCC_7H_{15})_2$	0.18[b]	2.1
$Pb(OOCC_7H_{15})_2$	0.14	0.8
$Cu(OOCC_7H_{15})_2$	1.2	1.2
$Zn(OOCC_9H_{19})_2$	0.35	1.8
Zn Naphthenate	1.3	4.5
Cd Naphthenate	0.6	not tested
Pb Naphthenate	0.16	0.9
Control	0.009	-

a   Catalyst Conc. 0.4% for PPG System; 0.2% for HTPB System

b   Catalyst not completely soluble in system

was 25% of the total binder. These two binders were selected because they are typical of materials currently being considered for solid rocket propellants and because they represent two extremes in reactivity and moisture absorption capability. The R-45 prepolymer yields a fast curing, comparatively water impermeable, hydrocarbon matrix, and PPG gives a slower curing binder which absorbs moisture readily. A catalyst concentration of 0.2% (regardless of whether or not the catalyst was completely soluble in the binder system) was selected because this corresponds to the average level of catalyst normally used in polyurethane propellants. Target crosslink density was 0.7×10^{-4} moles chains/cm^3. Cure was accomplished at room temperature. The specific formulations used for this study are:

PPG Binder	Weight %	HTPB Binder	Weight %
TP-2540	9.45	R-45	70.73
PPG	58.60	IDP	25.00
IDP	25.00	HDI	4.12
HDI	6.75	Neozone D	0.10
Neozone D	0.10		

The results are listed in Tables 8a and 8b. All of the HTPB binders, both catalyzed and uncatalyzed, cured if given sufficient time. By contrast, relatively few of the catalysts provided cure in the PPG binders. Those which appear to be most promising from these cure tests are $Fe(AA)_3$, $Mn(AA)_3$, $Th(AA)_3$, $Zn(AA)_2$, lead naphthenate and several of the tin compounds. The reason for this difference in cure behavior is believed to be the higher concentration of water present as impurity in the polyether diol, which can be orders of magnitude greater in PPG than in the HTPB. If the urethane catalyst also accelerates the water (urea) reaction, the effect will be a substantial deficiency of isocyanate groups for the binder network, since for every urea linkage two equivalents of isocyanate are consumed.

$2RNCO + H_2O \rightarrow RNHCONHR + CO_2$. As a rule incipient gelation of propellant

TABLE 8a

AMBIENT TEMPERATURE CURE OF CATALYZED HTPB BINDERS

(Binder: R-45/25% IDI/HDI, Catalyst Level 0.2%)

Catalyst	Cured After[a]	
	2 Hours	16 Hours
Control	-	-
$Fe(AA)_3$	+	+
$Mn(AA)_3$	+	+
$Mn(AA)_2$	-	-
$Co(AA)_3$[b]	-	-
$Co(AA)_2$[b]	-	-
$Ni(AA)_2$[b]	-	-
$VO(AA)_2$[b]	-	+
$V(AA)_3$[b]	-	-
$Cu(AA)_2$[b]	+	+
$Cd(AA)_2$[b]	-	-
$In(AA)_3$[b]	-	+
$Th(AA)_4$[b]	-	+
$Zn(AA)_2$[b]	+	+
$Pb(AA)_2$[b]	-	+
$Ce(AA)_3$[b]	-	-
$Ce(AA)_4$[b]	-	-
$MoO(AA)_3$[b]	-	-
$UO_2(AA)_2$[b]	-	-

a   All samples cured in 5 days at room temperature
b   Compounds not completely soluble

NOTE: Rather soft cures were obtained with $Ce(AA)_4$, $Ce(AA)_3$, $VO(AA)_2$, $Pb(AA)_2$, $Cd(AA)_2$ and control.

TABLE 8a (cont.)

Catalyst	Cured after[a]	
	2 Hours	16 Hours
$Bu_2Sn(OOCC_{11}H_{23})_2$	+	+
$(Bu_2SnS)_3$	+	+
$Cu(OOCC_7H_{15})_2$	-	+
$Pb(OOCC_7H_{15})_2$	-	+
$Sn(OOCC_7H_{15})_2$	-	+
$Cr(OOCC_7H_{15})_3$	-	-
$Zn(OOCC_9H_{19})_2$	-	+
Pb Naphthenate	-	+
Zn Naphthenate	-	+
Cd Naphthenate	-	-

TABLE 8b

AMBIENT TEMPERATURE CURE OF CATALYZED PPG BINDERS

(Catalyst level 0.2%)

	Cure 24 Hours	After 10 days[b]	Comments
$Fe(AA)_3$	+	+	good rubbery cure
$Mn(AA)_3$	+	+	good rubbery cure
$Mn(AA)_2$	-	-	waxy, non rubbery
$Co(AA)_3$[a]	-	-	greasy
$Co(AA)_2$[a]	-	(+)	very soft cure
$Ni(AA)_2$[a]	-	-	waxy, non-rubbery
$V(AA)_3$[a]	-	+	very sticky surface
$VO(AA)_2$[a]	-	+	very sticky surface
$Cu(AA)_2$[a]	+	+	very hard and brittle
$Th(AA)_4$[a]	+	+	good rubbery cure
$In(AA)_3$[a]	+	+	good rubbery cure
$Zr(AA)_4$[a]	-	-	waxy
$Al(AA)_3$[a]	-	-	greasy
$TiO(AA)_2$[a]	-	-	greasy
$Ca(AA)_2$[a]	-	-	greasy
$Mg(AA)_2$[a]	-	-	greasy
$Pb(AA)_2$[a]	-	(+)	very soft cure
$Zn(AA)_2$	+	+	good rubbery cure
$Cd(AA)_2$[a]	-	-	greasy

a   Not completely soluble.
b   After 10 days at room temperature the uncured specimens were placed into an oven for 48 hours. No further change took place indicating cure side reactions had taken place.

TABLE 8b (cont.)

	Cure 24 Hours	After 10 Days[b]	Comments
Bu_3SnCl	+	+	good rubbery cure
$Bu_2Sn(OOCCH_3)_2$	+	+	good rubbery cure
$Bu_2Sn(OOCC_{11}H_{23})_2$	+	+	good rubbery cure
$Bu_2Sn(OOCCH=)_2$	+	+	good rubbery cure
$(Bu_2SnS)_3$	+	+	good rubbery cure
$(Bu_2SnO)_x$[a]	-	-	waxy, non rubbery
$Bu_3SnOOCCH_3$[a]	-	-	waxy, non rubbery
Pb Octoate	+	+	good cure
Sn Octoate	+	+	good cure
Zn Octoate	+	+	good cure
Zr Octoate	-	-	grease-like consistency, non rubbery
Co(II) Octoate[a]	-	-	grease-like consistency, non rubbery
Ni Octoate[a]	-	-	grease-like consistency, non rubbery
Pb Naphthenate	+	+	good cure
Cd Naphthenate	-	+	good cure
Mg Naphthenate	-	-	grease-like consistency

---

a Not completely soluble

b After 10 days at room temperature the uncured specimens were placed into an 80°C oven for 48 hours. No further change took place indicating cure side-reactions had taken place.

binders occurs at about 92% reaction. Thus a few equivalent percent of
isocyanate consumed in nonnetwork forming side reactions can easily result
in cure failure. The amount of water necessary for this is about 0.04%. The
binders which were soft after 10 days at room temperature still failed to
cure when the temperature was increased to 80°C. Extensive isocyanate
decomposition or reaction with moisture had apparently taken place, since no
free isocyanate was detectable by infrared.

With several of the more promising catalysts binders were
prepared and their uniaxial tensile properties were determined. The catalyst
concentration in these binders was 0.1% in the polyether system and 0.05%
in the HTPB system. Two sets of each binder type were prepared; one set was
cured at 135°F, the other at room temperature. The results obtained in the
+135°F cure studies are shown in Tables 9 and 10. Many of the catalysts
tested provided satisfactory cures in the PPG binder at +135°F. However,
very poor mechanical properties were obtained with the $Cu(AA)_2$ and copper
octoate cured binders, and very poor aging stability with alkyltin compound
catalyzed rubbers. This is not apparent in the tin octoate catalyzed binder
(Table 9, aged data in parenthesis).

In some cases, like $Th(AA)_4$, cure failure in binders may
have been largely the consequence of its infinitesimal solubility in the pre-
polymers. If the binder containing the catalyst is frequently stirred or
shaken up during cure, to keep the catalyst homogeneously dispersed, the
specimen will cure. Similarly if the binder is dispersed with inert filler
(such as glass beads), the catalyst is kept in suspension and sample will cure.

In the R-45 HTPB binders, good cures were obtained in almost
every case. Surface hardening is the most pronounced phenomenon, which is
greatly aggravated by some of the catalysts. The worst offenders are Cu, Co,
V, Mn and Fe compounds.

TABLE 9

MECHANICAL PROPERTIES OF POLYETHER BINDERS (135°F Cure)

Catalyst	Sol Fraction[b] %	v_2	Crosslink Density $(\nu_e/V_o)10^4$	Uniaxial Tensile Properties[f] σ_m psi	ε_b %	E_o psi
$Fe(AA)_3$	2	.129	1.10	88 (70	197 205	127 85)[c]
$Bu_2Sn(OCOC_{11}H_{23})_2$[e]	6	.110	0.81	127 (>34[d]	410 >710	88 44)
$Bu_2Sn(OCOCH_3)_2$[e]	11	.125	1.05	>79 (7	>300 414	117 4)
$(Bu_2SnS)_3$[e]	11	.118	.92	>88 (>17	>350 >640	94 10)
$Mn(AA)_3$	6	.129	1.10	95 (95	244 377	110 83)
$Sn(Oct)_2$	4	.125	1.05	144 (132	407 424	125 110)
$Cu(AA)_2$[a]	9	.140	1.31	37 (41	52 41	110 121)
$Cu(Oct)_2$	7	.140	1.31	54 (31	102 135	88 79)
Cd Naphthenate	11	.105	0.75	>87 (100	>414 638	81 66)
$Pb(Oct)_2$	2	.125	1.05	102 (88	256 552	127 76)
Pb Naphthenate	4	.110	0.81	130 (90	456 515	101 66)
$Pb(AA)_2$[a]	8	.099	0.68	>94	>537	73
$Th(AA)_4$[a]			-- not measurable --			
$Zn(AA)_2$[e]	12	.118	0.92	>109 (>129	>484 >630	87 75)
$Co(AA)_2$[ae]	11	.114	0.87	>113 (>91	>474 >650	79 55)
$Ni(AA)_2$[ae]	10	.108	0.78	67 (73	319 415	66 62)

a   Catalyst not completely soluble, in case of $Th(AA)_4$ only lower half of bar cured.
b   Swelling in benzene for 5 days with 3 changes of solvent.
c   Numbers in () refer to aged binders (4 weeks at 80°C in air).
d   The > sign in front of number indicates that failure value is larger. Sample either failed to break within crosshead limit, or slipped from jig during stretch.
e   Tacky surface of weakly cured specimen.
f $\dot{\varepsilon} = 7.4$ min^{-1}

TABLE 10

MECHANICAL PROPERTIES OF R-45/IDP BINDERS (Cure at 135°F)

Catalyst	Sol Fraction %	v_2	Uniaxial Tensile[c] Properties at 77°F		
			σ_m, psi	ε_b, %	E_o, psi
Fe(AA)$_3$[c]	33	.122	35 (85	246 20	45 1280)[d]
Bu$_2$Sn(OCOC$_{11}$H$_{23}$)$_2$	31	.098	30 (38	338 239	37 49)
Bu$_2$Sn(OCOCH$_3$)$_2$	33	.102	34 (38	335 215	38 51)
(Bu$_2$SnS)$_3$	35	.097	32 (40	448 253	31 51)
Mn(AA)$_3$[a,c]	41	.092	19 (24	226 17	37 516)
Sn(Oct)$_2$	39	.098	30 (36	354 226	42 44)
Cu(AA)$_2$[a,c]	37	.084	21 (28	387 7	37 806)
Cu(Oct)$_2$[c]	40	.084	16 (43	340 5	42 1050)
Cd Naphthenate	40	.084	>21 (24	>555 263	26 40)
Pb(Oct)$_2$[c]	32	.118	27 (33	500 261	42 44)
Pb Naphthenate	42	.081	>19 (25	>540 239	31 51)
Th(AA)$_4$[a]	42	.076	11 (20	321 229	29 40)
Zn(AA)$_2$[a]	40	.078	16 (27	513 301	20 40)
Co(AA)$_2$[a,c]	43	.085	>13 (42	>556 5	31 996)
Ni(AA)$_2$[a]	43	.091	14.5 (23	529 316	33 40)
VO(AA)$_2$[a,c]	41	--	21 (47	384 4	19 1380)
Control[b]	37	.085	13 (20	543 262	31 57)

a   Catalyst not completely miscible
b   5 days cure, all others 2 days
c   Extreme surface hardening, during aging
d   Properties after 4 weeks aging at 80°C
e $\dot{\varepsilon} = 7.4$ min^{-1}

Data for the room temperature cured binders are presented in Tables 11 and 12. Aging data have not been obtained on these specimens, mainly because only a few catalysts in the PPG series gave satisfactory cures, and secondly it is felt that no new knowledge would be gained. Swelling data were not obtained, for similar reasons.

In the PPG binders the only well cured specimens were obtained with $Fe(AA)_3$, lead naphthenate and lead octoate. The next best catalyst was tin octoate. Copper catalyzed binders ($Cu(AA)_2$ and copper octoate) cured well but the mechanical properties of the resulting elastomers are very poor.

The catalysts which gave cures at 135°F but not at room temperature were $Mn(AA)_2$, $Co(AA)_3$, $Co(AA)_2$, $Ni(AA)_2$, $V(AA)_3$, $Cd(AA)_2$, $Ce(AA)_3$, $Ce(AA)_4$, $MoO(AA)_3$, $UO_2(AA)_2$, $Cr(OOCC_7H_{15})_3$ and cadmium naphthenate. Again, none of the specimens that failed to cure at room temperature could be cured subsequently by raising the cure temperature. This indicates that side reactions have taken place while the samples were stored at room temperature.

In the HTPB system, all catalysts promoted cure. Cure failures were not encountered, but it should be noted that even the un-catalyzed mixture of the reactants eventually cures. The tacky surface (indicative of moisture interference) so common in polyether binders is usually absent in the HTPB binders.

4. Catalyst Screening by Propellant Cure Studies

Catalysts were also evaluated in propellant formulations. The propellants selected contain 84 wt% total solids (69 wt% ammonium perchlorate and 15 wt% aluminum). The propellant binders were the same ones used for the gumstock studies, and the catalyst concentration was 0.3%.

The results obtained in these screening tests were essentially the same as those reported for the gumstock studies. All propellants

TABLE 11

MECHANICAL PROPERTIES OF PPG BINDERS
CURED 5 DAYS AT ROOM TEMPERATURE

Catalyst	Uniaxial Tensile Properties at +77°F[d]		
	σ_m, psi	ϵ_b, %	E_o, psi
$Fe(AA)_3$	147	416	127
$Mn(AA)_3$[a]	88	488	81
$Cu(AA)_2$	55	69	134
$Zn(AA)_2$[b]	>91	>538	94
$Bu_2Sn(Ac)_2$[b]	>68	>353	88
$Bu_2Sn(OCOC_{11}H_{23})_2$[b]	>67	>374	90
$(Bu_2SnS)_3$[c]	>68	>451	70
$Pb(Oct)_2$	>95	>654	83
$Sn(Oct)_2$[a]	80	355	121
Pb Naphthenate	83	573	83

a = tacky surface

b = very tacky

c = liquid layer on top

d $\dot{\epsilon} = 7.4 \, min^{-1}$

(such specimens usually slip through the jig during testing)

NOTE: Binders catalyzed with zinc naphthenate and decanoate were so tacky and poorly cured, that they were discarded.

TABLE 12

MECHANICAL PROPERTIES OF R-45 HTPB BINDERS
CURED 5 DAYS AT ROOM TEMPERATURE

Catalyst	Uniaxial Tensile Properties at +77°F[a]		
	σ_m, psi	ϵ_b, %	E_o, psi
$Fe(AA)_3$	27	142	55
$Bu_2Sn(OCOC_{11}H_{23})_2$	35	250	66
$(Bu_2SnS)_3$	41	219	62
$Mn(AA)_3$	38	371	62
$Cu(AA)_2$	30	307	55
Pb Octoate	21	357	44
$Th(AA)_4$	12	117	35
$Zn(AA)_2$	21	381	51
$Co(AA)_2$	12	218	27
$Ni(AA)_2$	8	324	20
Control	3	521	4

[a] $\dot{\epsilon} = 7.4$ min^{-1}

made with the R-45 HTPB binder cured at ambient temperature if given
sufficient time. Only those PPG propellants catalyzed by $Fe(AA)_3$, $Cu(AA)_2$,
$Pb(AA)_2$, dibutyltin dilaurate, tin octoate, lead octoate and lead naphthenate
cured. These catalysts are believed to be good candidates to promote the
cure of HTPB propellants at room temperature. A summary of all the catalysts
tested and the cure behavior of the PPG propellants prepared is shown in
Table 13.

The consumption of isocyanate by water, and possible catalyst
degradation by moisture, are the most probable causes of cure failure in the
PPG propellants. In some instances, the cause of cure failure can be ascer-
tained from the appearance of the uncured propellant. For example, if the
visual appearance and flow properties of the propellant do not change
appreciably with time (after casting), this can be attributed to catalyst
degradation, the use of an ineffective catalyst, or absence of catalyst. In
these cases, the addition of a fresh, potent catalyst like $Fe(AA)_3$ will cause
cure of such a propellant, if the cure time prior to FeAA addition was not
too long. Cure cannot be effected, even in an uncatalyzed PPG
propellant, by $Fe(AA)_3$ addition after seven days standing time at room
temperature (Control, Table 13), as a result of slow consumption of isocyanate
by side reactions.

Several examples of cure failure due to relatively ineffective
catalysis can be seen for $TiO(AA)_2$, $Cr(AA)_3$, $Co(AA)_3$ (Table 13). At the con-
centrations tested, none of these catalysts effected cure.

Propellants in which cure failure is due to side reactions
of the isocyanate with moisture usually become semisolid and have the
appearance of fudge, i.e., dry, crumbly, noncoherent masses. Often the volume
of such propellants has increased due to the formation of CO_2 from the water-
isocyanate reaction. Examples of catalysts which appear to promote the water-iso-
cyanate reaction (Table 13) are $Zn(AA)_2$, zinc naphthenate and decanoate, cadmium

TABLE 13

AMBIENT TEMPERATURE CURING OF PPG TYPE PROPELLANTS PREPARED WITH VARIOUS CATALYSTS

| | State of Cure | | | | |
| | Ambient Temperature | | Effect of FeAA Addition After The Indicated Days Ambient Cure | | |
Catalyst	1 Day	5 Days	1 Day	2 Days	7 Days
Fe(AA)$_3$	c	-	-	-	-
Mn(AA)$_3$	nc,(d)	nc,(d)	nc	-	-
Co(AA)$_3$	nc,(d)	nc,(d)	c	c	nc
Cr(AA)$_3$	nc,(d)	nc,(d)	c	c	nc
Ce(AA)$_3$	nc,(d)	nc,(d)	nc	-	-
V(AA)$_3$	nc,(d)	nc,(d)	nc	-	-
In(AA)$_3$	nc,(d)	nc,(d)	nc	-	-
Th(AA)$_4$	nc,(d)	nc,(d)	nc	-	-
Zr(AA)$_4$	nc,(d)	nc,(d)	nc	-	-
UO$_2$(AA)$_2$	nc,(d)	nc,(d)	nc	-	-
MoO(AA)$_3$	nc,(d)	nc,(d)	nc	-	-
VO(AA)$_2$	nc,(d)	nc,(d)	nc	-	nc
TiO(AA)$_2$	nc,(1)	nc,(1)	c	c	nc
Mn(AA)$_2$	nc,(d)	nc,(d)	nc	-	-
Co(AA)$_2$	nc,(d)	nc,(d)	nc	-	-
Ni(AA)$_2$	nc,(d)	nc,(d)	nc	-	-

c   = cured
nc   = no cure,
nc,(d) = no cure but dry fudge like appearance (no longer castable)
nc,(1) = no cure, but liquid appearance (castable)

TABLE 13 (Cont.)

State of Cure

Catalyst	Ambient Temperature		Effect of FeAA Addition After The Indicated Days Ambient Cure		
	1 Day	5 Days	1 Day	2 Days	7 Days
$Pb(AA)_2$	nc,(l)	c	c	c	nc
$Cd(AA)_2$	nc,(d)	nc,(d)	nc	nc	-
$Zn(AA)_2$	nc,(d)	nc,(d)	nc	nc	-
Ni Octoate	nc,(d)	nc,(d)	nc	nc	-
Pb Octoate	nc	c	-	-	-
Cu Octoate	c	c	-	-	-
Sn Octoate	c	c	-	-	-
Zn Decanoate	nc,(d)	nc,(d)	-	-	-
Pb Naphthenate	nc	c	-	-	-
Zn Naphthenate	nc,(d)	c	nc	nc	-
Cd Naphthenate	nc,(d)	nc	nc	nc	-
$Bu_2Sn(OCOC_{11}H_{23})_2$	c	c	-	-	-
$Bu_2Sn(OCOCH_3)_2$	nc,(d)	nc,(d)	-	-	-
$(Bu_2SnS)_2$	nc,(d)	nc	nc	nc	-
Control	nc,(l)	nc,(l)	c	c	nc

c = cured
nc = no cure
nc,(d) = no cure but dry fudge like appearance (no longer castable)
nc,(l) = no cure, but liquid appearance (castable)

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naphthenate, $Zr(AA)_4$ and $MoO(AA)_3$. Several infrared spectra have been obtained which corroborate these conclusions (Figures 4 to 6).

Figure 4 shows the spectrum of a stoichiometric PPG-HDI mixture before any significant degree of reaction has taken place. In Figure 5 the spectrum of the PPG-urethane which was obtained by reacting PPG with butyl isocyanate is shown. Figure 6B is the spectrum of a room temperature saturated, ternary system, $PPG/H_2O/AP$, which was obtained by stirring PPG with a saturated aqueous solution of ammonium perchlorate. The spectrum of the liquid layer on top of a PPG-HDI propellant that failed to cure is shown in Figure 6A. Note that the NH peak is higher, and the carbonyl peak lower than in Figure 5, and that there the inflection in the NH band is still evidence of OH. The carbonyl peak has become more complex since the product now contains carbamate and urea carbonyls. The latter actually has two peaks (1630 and 1670 cm^{-1}) of which only the one (1630 cm^{-1}) is clearly seen, the other being obscured by the carbamate carbonyl. In addition, peaks attributed to ammonium perchlorate by comparison with the spectrum in Figure 6A are seen at 3200 and 3050 cm^{-1}. From all three spectra, it appears that the effects of simple catalyst degradation and moisture interference can be differentiated by infrared.

C. NETWORK EFFECTS

1. General Comments

Optimum properties of a given propellant matrix are obtained if no inert diluents, such as plasticizers, loose chain ends, as are produced by improper cure or a poor quality of prepolymers, are present. The most important single parameter of a propellant binder is its strain capability. Strain capability is proportional to $\sqrt{M}$, the molecular weight of chains between branch points.[12] Consequently, a propellant binder should have the lowest possible crosslink density, that can be safely attained. For most

INFRARED SPECTRUM OF PPG-HDI MIXTURE
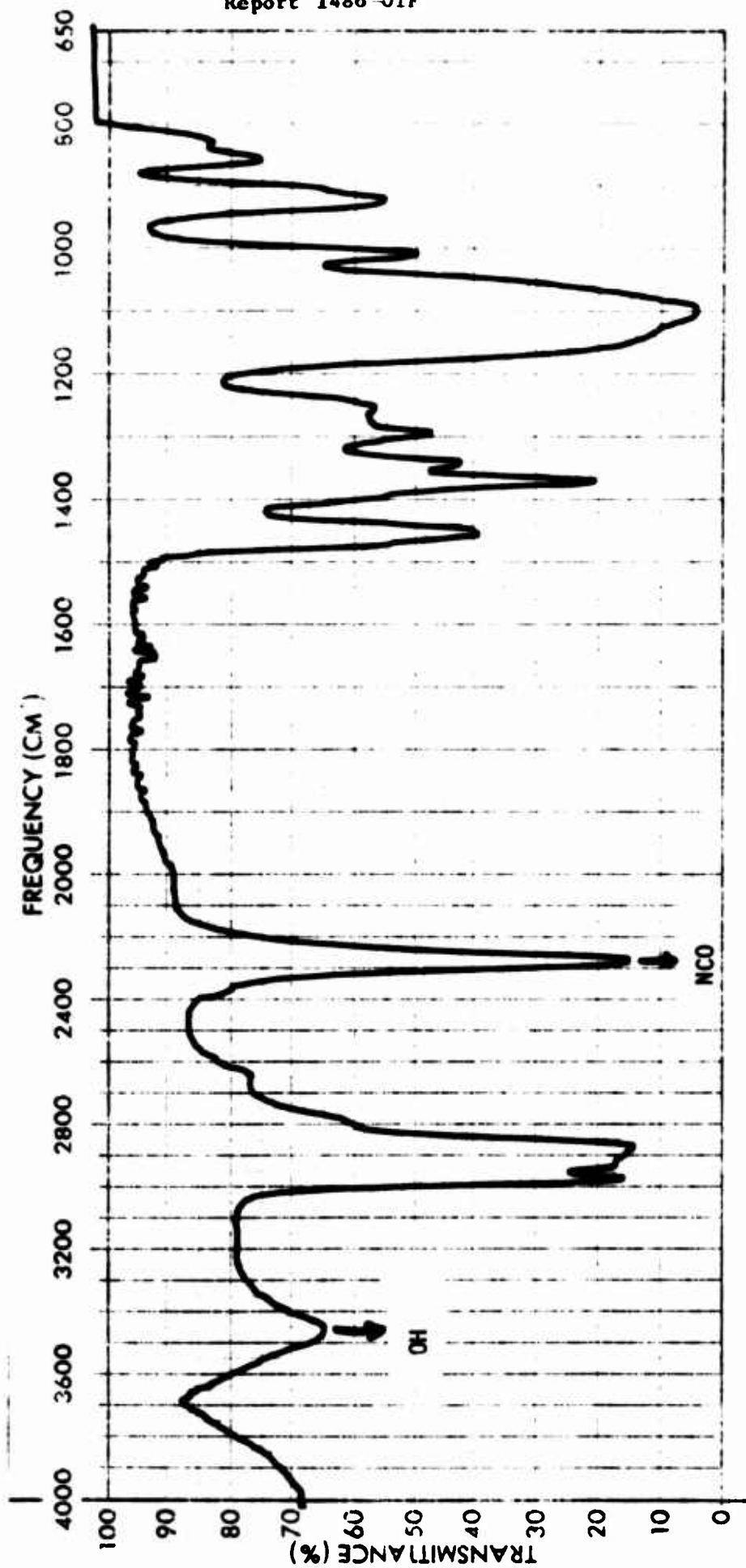
Figure 4

INFRARED SPECTRUM OF REACTED PPG AND BUTYL ISOCYANATE
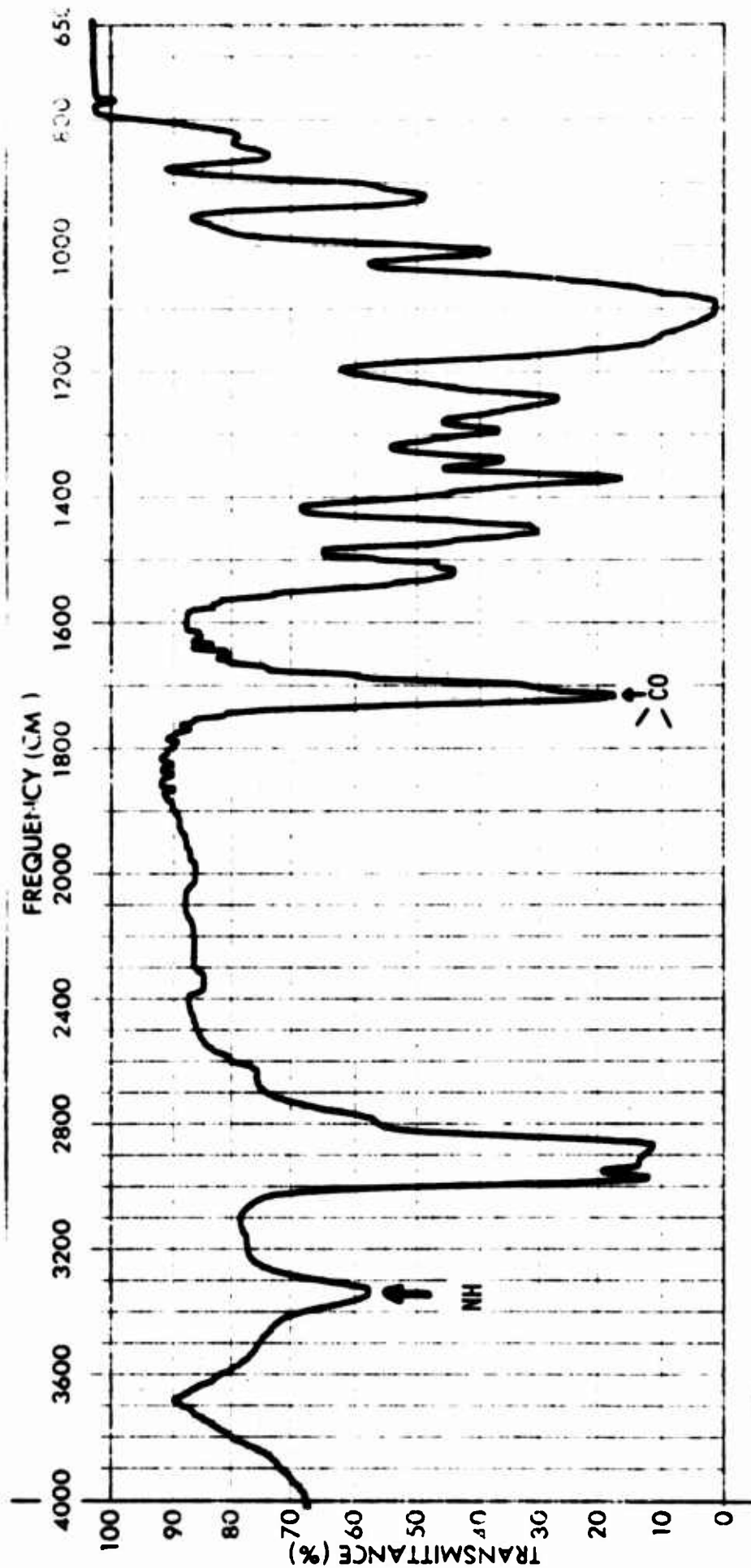
Figure 5

A - SUPERNATANT LIQUID FROM PROPELLANT
(Cd naphthenate catalyst) that failed to cure

B - SATURATED AP/H$_2$O/PPG SOLUTION
(14% AP, 15% H$_2$O, 71% PPG)

Figure 6
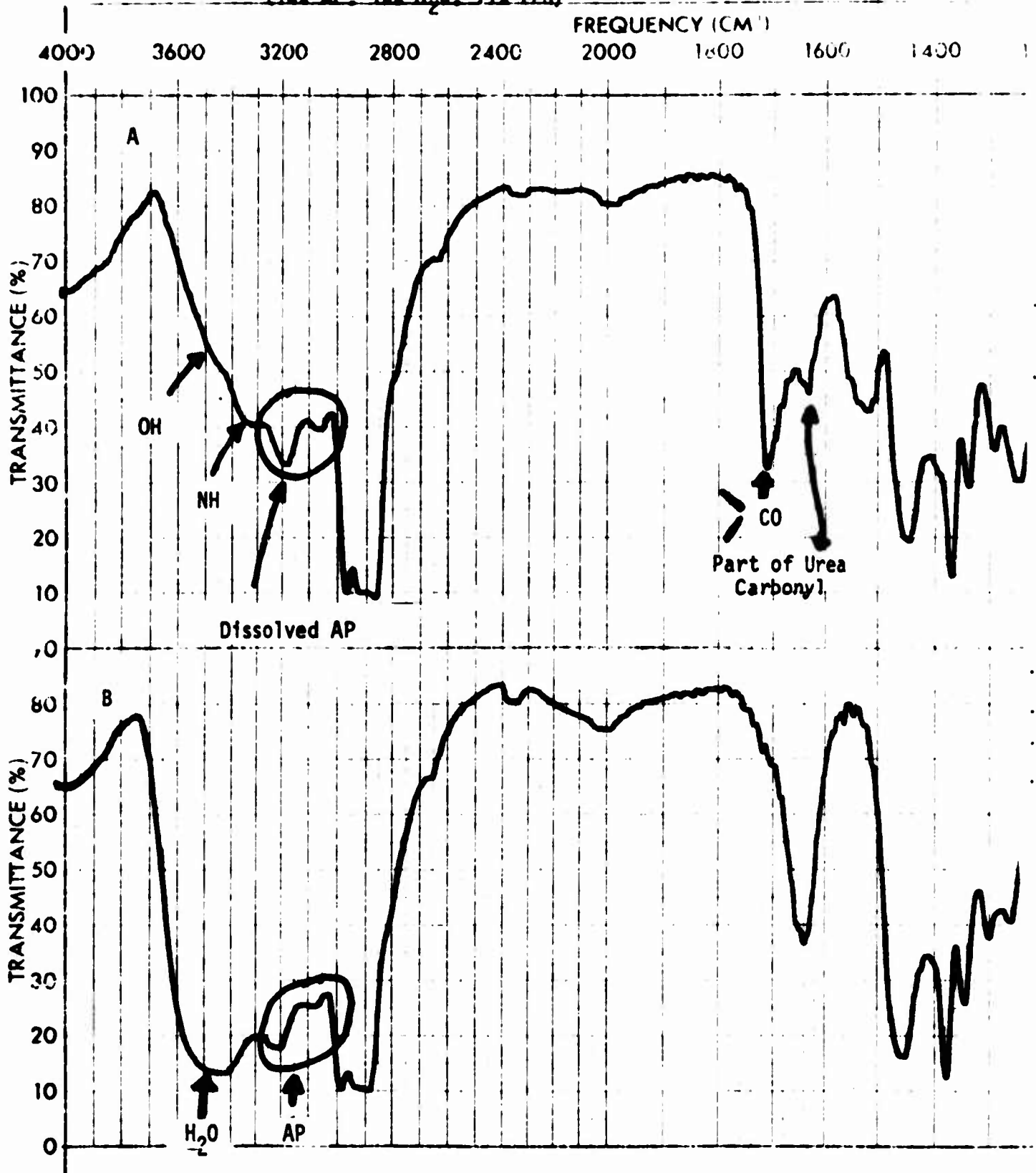
propellants this crosslink density is between 2 to 5 x 10^{-5} moles chains per cm^3, corresponding to molecular weights of the undiluted rubber of 50,000 to 20,000 respectively. Below 2 x 10^{-5} moles chains/cm^3 danger of cure failure and insufficient propellant strength become dominant. A low propellant modulus is usually associated with a low crosslink density, but this is not necessarily true. Plasticization and semiconnected chains will drastically lower the modulus without concomitant increase in strain capability.[13,14] This situation is shown in Figure 7. The effective strain is here defined as the strain that specimens will sustain for an indefinite length of time without failure. The effective strain is directly related to the onset of strain dilation in composite materials. Figure 8 shows the effect of plasticization and chain termination on tear energy. It is obvious that at the same cross-link density the energy required to tear the binder is much higher for the properly crosslinked binder than for those in which crosslink density has been reduced by chain scission or plasticization.

Another factor that is intimately affected by chain length is the stress decay or stress relaxation of rubbers. Although stress decay in one way is a nuisance as far as stress calculations of grain configurations are concerned, it is an undeniable fact that the best propellants, mechanical property wise, also exhibit the highest stress relaxation. Stress relaxation may be operative in reducing mometary peak stresses and thus preventing rupture of the composite. A convenient way of reporting the magnitude of stress relaxation is depicted in Figure 9. If the reduced stress (i.e. stress at time t, divided by a suitable reference stress, e.g. stress after 1 min. relaxation) is plotted vs. time it is observed that relaxation curves from specimens stretched to various elongations will form a single curve. If the reference stress, σ_R, is chosen at a time which is long compared to the time it took to stretch the specimen, then the relative stress decay D_R defined as $D_R = (\sigma_R - \sigma_t)/\sigma_R$, becomes practically independent of elongation, gage length and strain rate. For example D_{20} signifies $(\sigma_1 - \sigma_{20})/\sigma_1$ where the subscripts are minutes from the start of relaxation.

ON EFFECTIVE STRAIN
Polyurethane Rubber Filled with 40% Glass Beads
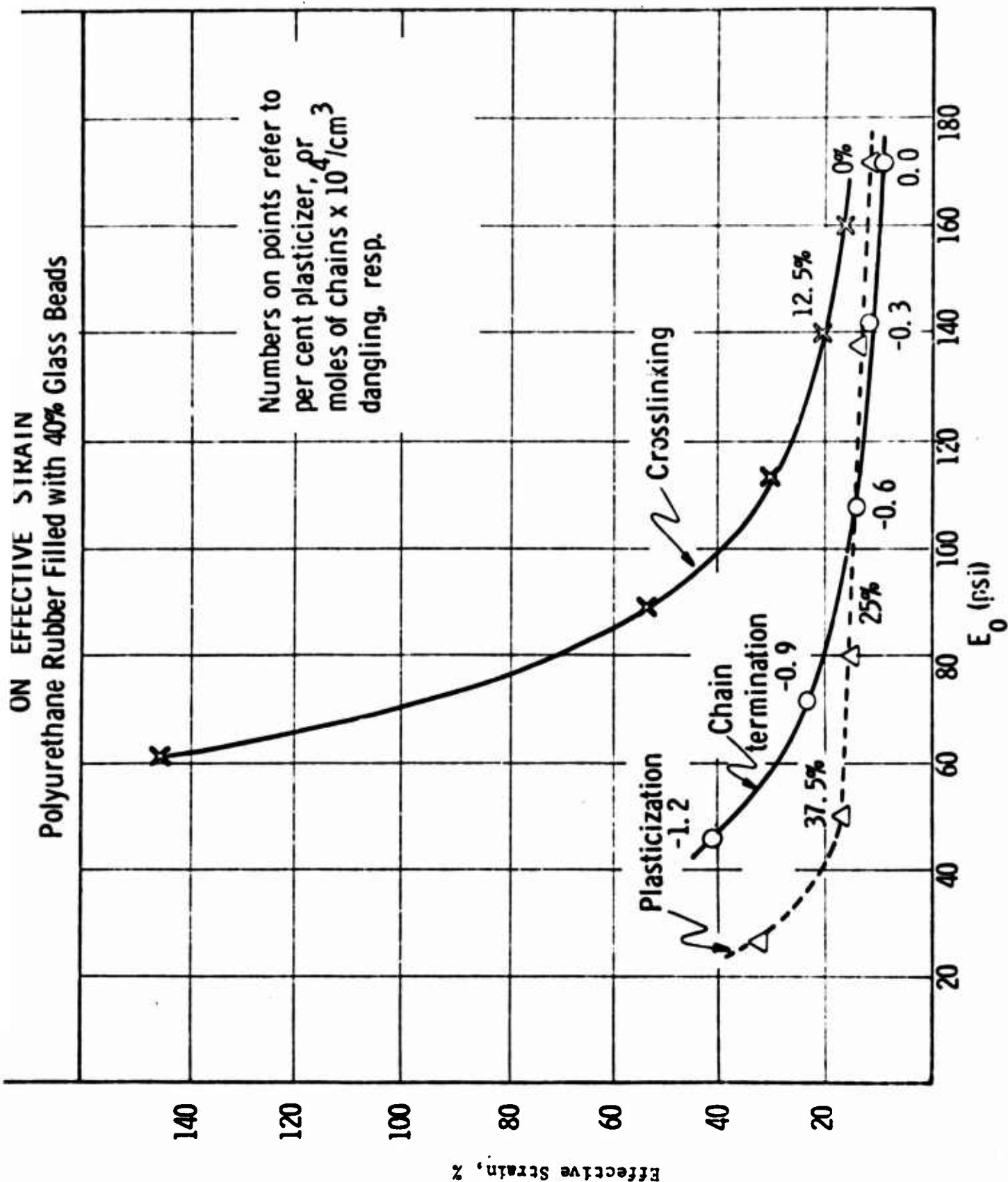
Figure 7

COMPARISON OF TEAR ENERGY WITH CROSSLINK DENSITY
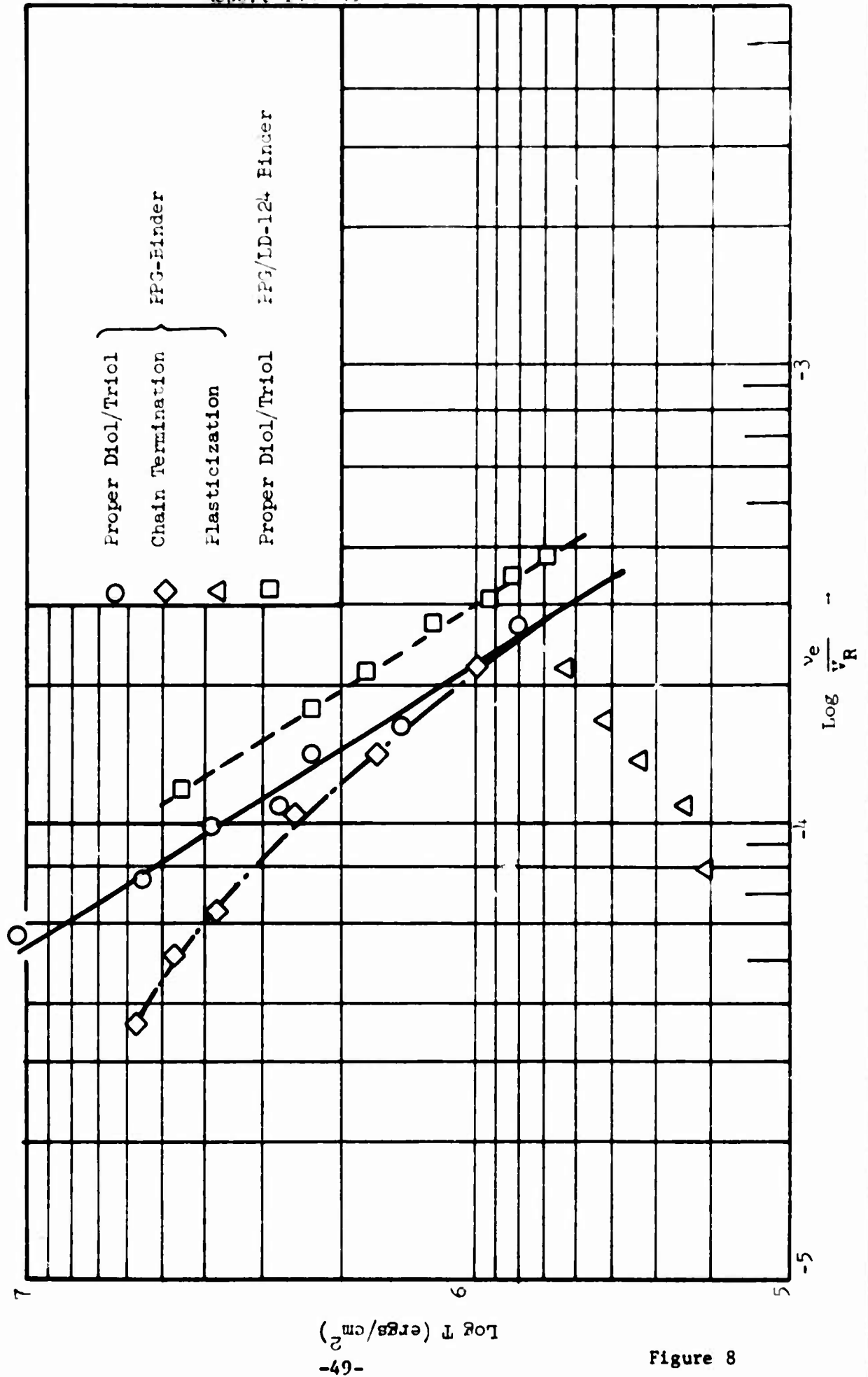
Figure 8

NORMALIZED STRESS DECAY AT LOW DEFORMATION IN
FILLED POLYURETHAN RUBBER 50 Vol. % Glass Beads
$T = 25^0$
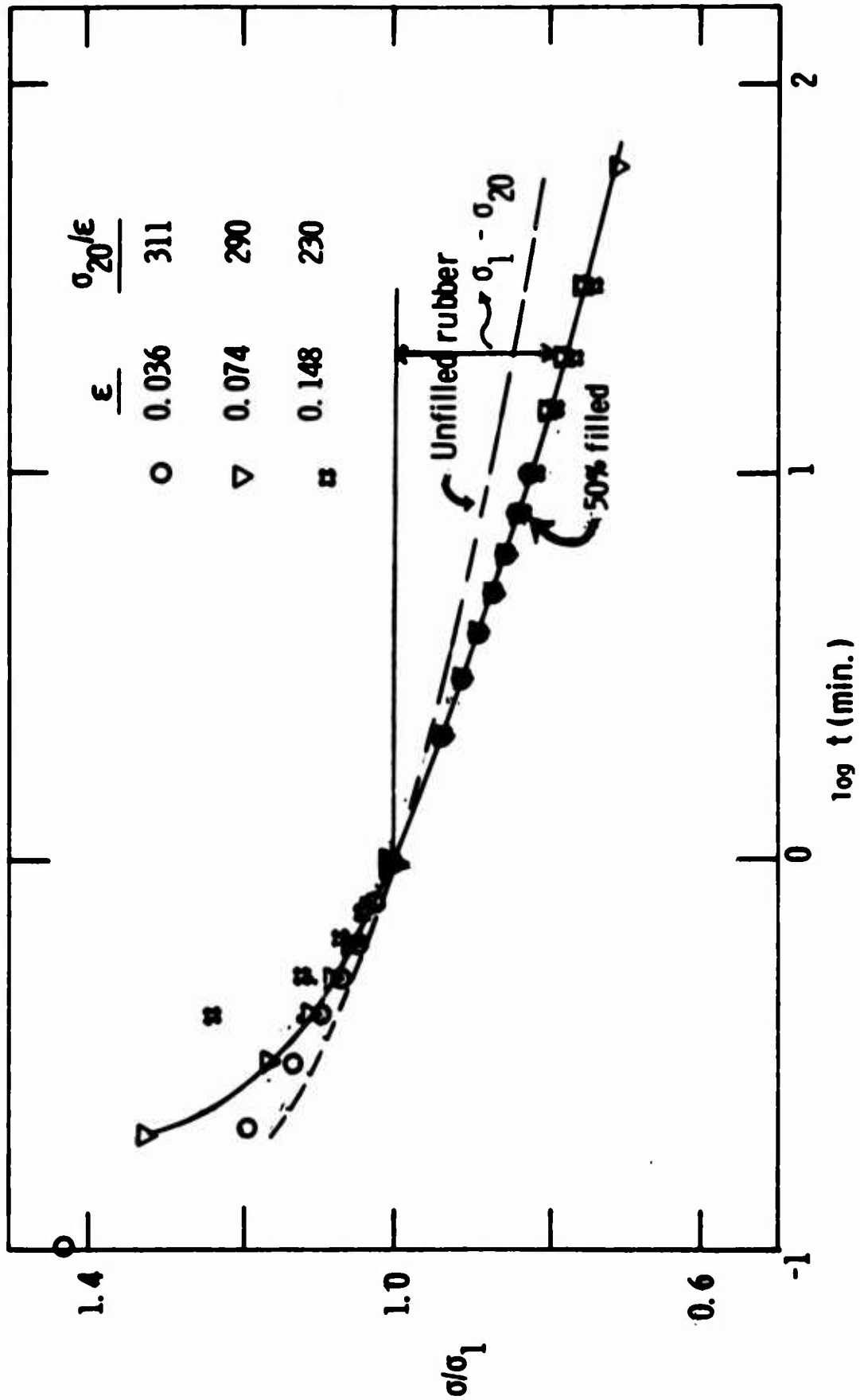
Figure 9

Figure 10 shows the stress decay for some binder types of varying crosslink density. It is obvious that chain termination yields only slightly relaxing rubbers. The effect of fillers on stress decay is shown in Figure 11. D_R in strongly relaxing binders is not affected by fillers, while it differs for weakly relaxing matrixes. The reason for this deviation is unclear.

If the functionality of the binder components are known, and if we can assume that stoichiometry of the cure reaction is fulfilled, then the theoretical crosslink density ν_{th} of the cured binder is given by

$$\nu_{th} = \frac{3d}{2} \sum_{i=1}^{n} \frac{(f_i - 2)}{f_i} \frac{W_i}{E_i} \tag{10}$$

where d is the density of the cured rubber, f_i is the functionality of the i_{th} component in the binder and may assume values between 1 and 3, W_i is its weight fraction, and E_i is the analytically determined equivalent weight. The equation is based on the following considerations. Of an f functional compound two functions are used for chain propagation. Therefore, $(f-2)/f$ represents the fraction of the functional groups which is available for crosslinking. The crosslink density will be proportional to the weight fraction of the particular component and inversely proportional to its equivalent weight. Only those prepolymers contribute to the over-all crosslink density whose functionality differs from 2.0. Plasticizers (f=0) are to be excluded since they are not part of the rubber network. However, they modify the weight fraction of the functional components. The factor 3d/2 converts the crosslink density from moles branch points/gram to the more familiar moles chains/cc. In the absence of diluents the average molecular weight between branch points is

$$M_c = \frac{1}{\nu_{th}} \tag{11}$$

STRESS DECAY OF SOME POLYURETHANE RUBBERS

Figure 10

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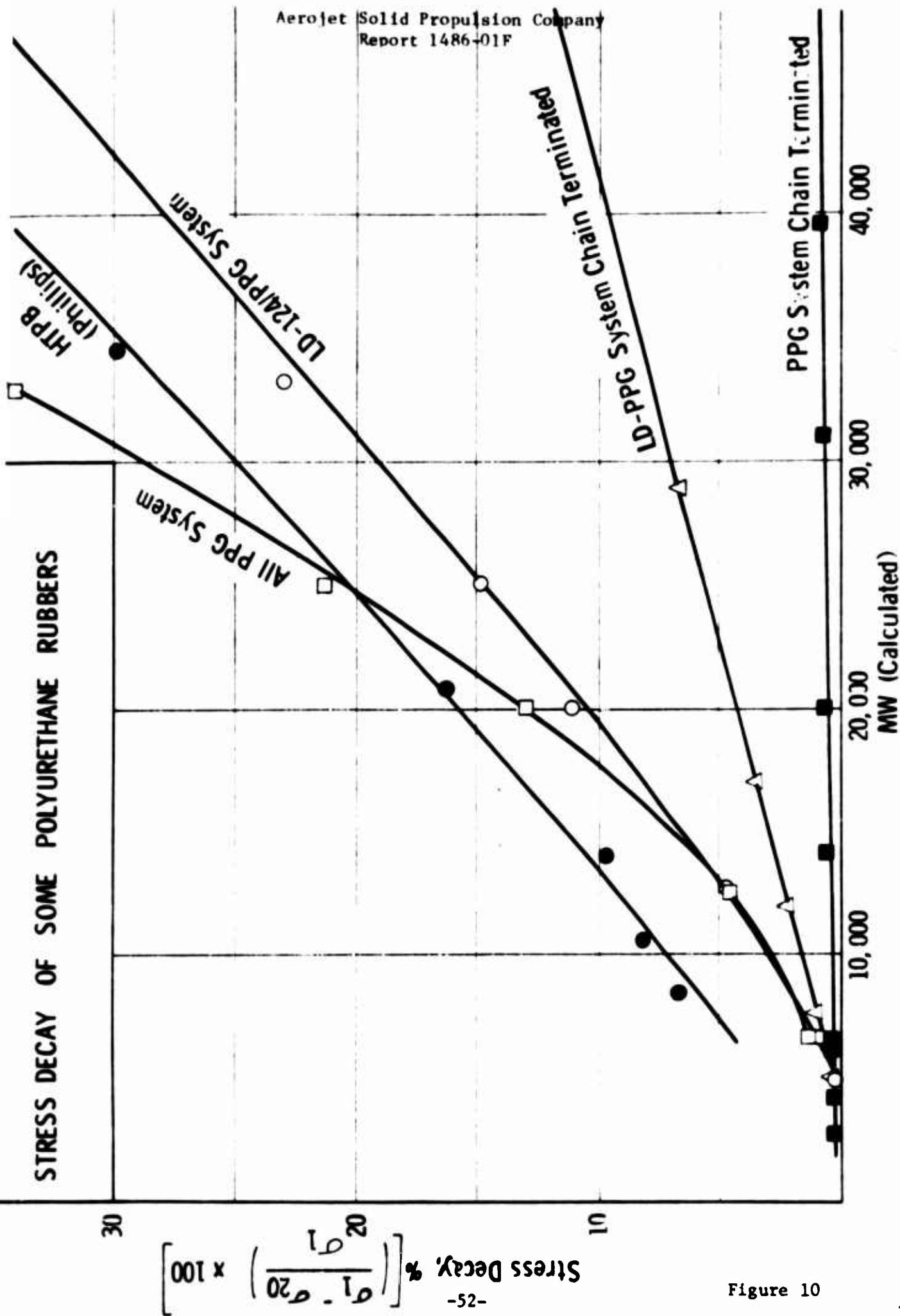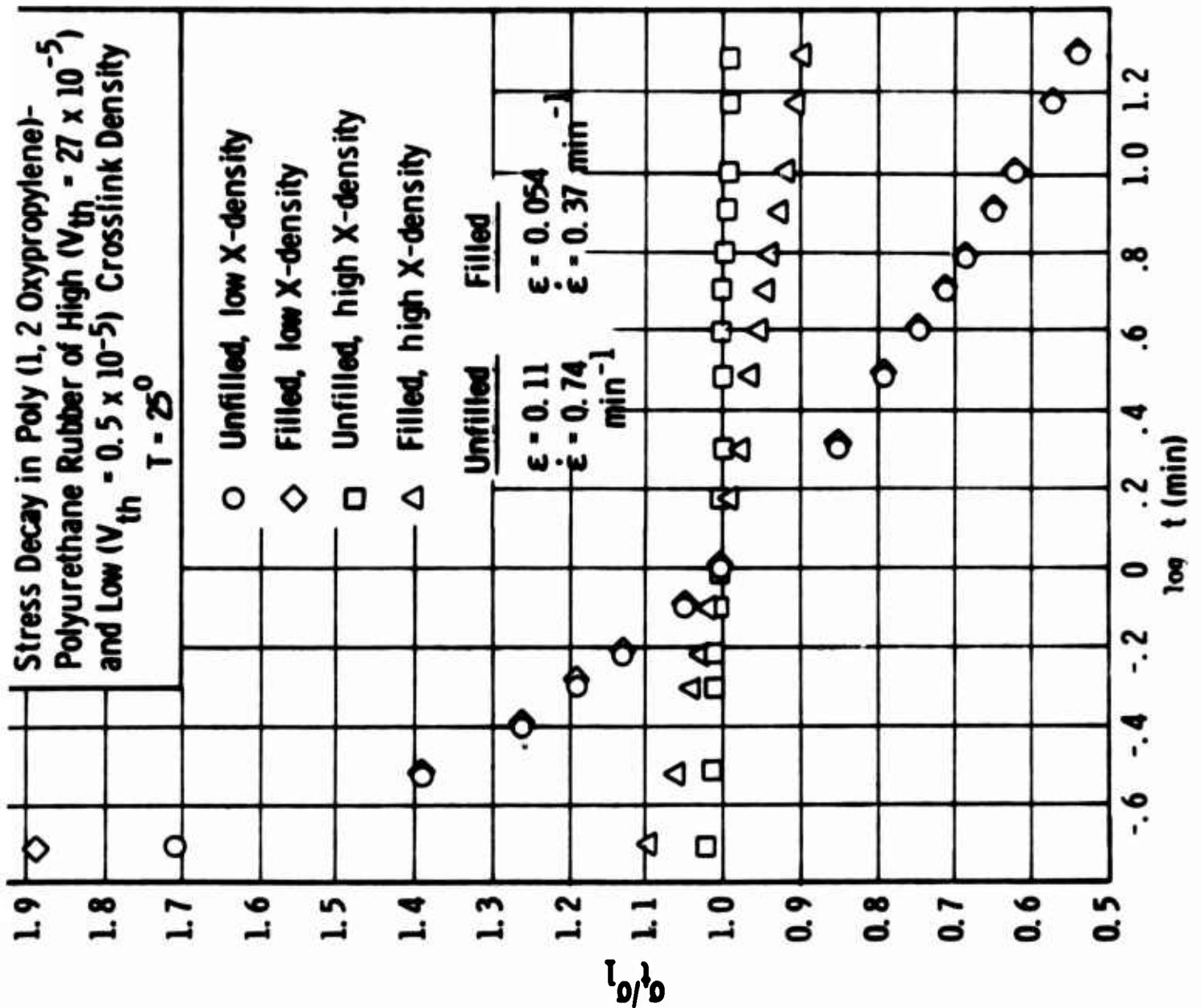
Figure 11

From the theory of elasticity the retractive force, τ, in uniaxial tension is given by

$$\tau = \nu_e RT(\alpha - \alpha^{-2}) \tag{12}$$

where ν_e is the moles of effective network chains, i.e. chain segments which terminate in branch points. Dangling or semiconnected chains are not included, since they do not support load. If ν_s designates the number of moles of semiconnected chains, ν_o the total moles of chains, τ, according to Flory[15] could be given by

$$\tau = (\nu_o - \nu_s)RT(\alpha - \alpha^{-2}) \tag{13}$$

It was, however, found[14] experimentally that the effect of nonload bearing structure on mechanical properties is considerably larger and equal to that of an equal volume fraction of plasticizer. Empirically, τ, may be represented approximately by

$$\tau = \nu_o RT(\alpha - \alpha^{-2})v_{s,p}^2 \tag{14}$$

where $v_{s,p}$ is the volume fraction of semiconnected chains, plasticizer or both.

2.   Cure Side Reactions

Obviously, failure of cure indicates that the stoichiometry of the hydroxyl-isocyanate reaction has been disturbed, usually resulting in leftover hydroxyl groups. In terms of cure or mechanical properties this means dangling unconnected chain ends whose effect on physical properties is twofold, a reduction of the quantity of load bearing structure leading to mechanically weak propellants and an effective reduction of crosslink

density which is the primary source of cure failure. The fact that $Fe(AA)_3$ and some of the other catalysts generally promote cure does not necessarily indicate that the cure reaction proceeds 100 percent in the desired direction, it only indicates that less of the isocyanate consuming side reactions occur. It is clear that in order to obtain optimum properties such side reactions should be avoided or brought under control. The two most important causes of cure failure are probably the moisture interference reaction and consumption of isocyanate by homopolymerization. Another, very recently discovered phenomenon is the effect of chain length distribution on mechanical properties. Per se, this effect may not cause failure to cure but it can markedly affect propellant reproducibility.

a. Theoretical Estimation of the Level of
Side Reactions which may Cause Cure Failure

Experience has shown that in order to obtain propellant cures a crosslink density of about $2-5 \times 10^{-5}$ moles of trifunctional branch points per gram rubber matrix (corresponding to 3 to 7×10^{-5} moles chains/cm^3 in a PBD matrix) is required.

Homopolymerization as well as moisture interference (urea formation) will consume isocyanate. This isocyanate will not be available for completing the cure reaction, so that the net effect is chain termination. Neither the moisture reaction nor homopolymerization (trimerization) per se will produce unconnected chain ends, since one mole of water will always react with two equivalents isocyanate to form one urea linkage, and trimerization consumes three equivalents NCO to form one crosslink. The point is that the quantity of isocyanate thus consumed will vary depending on the environmental conditions and cannot be readily accounted for in the calculation of the required quantity of diisocyanate in a propellant formulation. The effect of insufficient isocyanate on crosslink density for the case of small levels of termination can be calculated from Equation 10

which takes the form

$$v_t = - \frac{3d}{2} \frac{\Delta W_{DI}}{E_{DI}} \tag{15}$$

where ΔW_{DI} is the difference between the stoichiometrically required weight fraction of diisocyanate and the actual weight fraction. Each isocyanate group of the diisocyanate missing from the stoichiometric quantity will leave one unconnected chain end. Therefore v_t is a negative increment, which has to be deducted from the overall crosslink density. For every urea linkage formed one crosslink is destroyed and for every trimer crosslink, three other links will not be formed, if one started with stoichiometric quantities of hydroxyl and isocyanate groups. This somewhat oversimplified treatment considers only the effect which chain termination will have on cure, it does not account for its effect on mechanical properties.[14]

Two simple cases may be considered to demonstrate the effect of side reactions on the overall propellant cure. Assume the theoretical crosslink density v'_{th} = 5 x 10^{-5} moles branch points/g*. Hence in 100g of a 88 wt% loaded propellant there are 6 x 10^{-4} moles branch points. In order to neutralize these, an equal molar quantity of chain terminator is required. In case of moisture interference (since one mole of water consumes two equivalents isocyanate) 9 x 6 x 10^{-4} = 0.0054g H$_2$O/100g propellant are required. This quantity is just slightly above the surface moisture content of oxidizer stored with bags of drying agents (usually surface moisture of unground AP is between 0.002 and 0.003%). At present it is not known to what extent this moisture will enter into the cure reaction.

In the second case we want to find out what percentage of the isocyanate of the propellant batch, if trimerized, will suffice to offset crosslinking. Here three NCO groups will be removed and one crosslink

*v'_{th} is related to v_{th} by $v_{th} = 3dv'_{th}/2$

formed. The simplified net effect is two terminations per three trimerizing NCO groups. Hence, for the above case $(3/2) \times 84 \times 6 \times 10^{-4} = 7.6 \times 10^{-2}$ grams of HDI must trimerize to cause cure failure. The level of HDI in such propellants is around 0.5%, therefore if $0.076/0.5 = 15$ percent of the HDI trimerizes cure failure may occur if no provision for such an effect is taken. It will be shown later that the magnitude of such effects are easily within the range of encountered homopolymerization. Thus moisture effects and isocyanate selfcondensation reactions can readily account for the observed cure failures.

In most propellants, a slight excess of NCO over OH is used probably to counteract such reactions. In well curing systems, excess isocyanate may, however, result in additional crosslinking as a result of trimerization.

b.   Moisture Interference Reaction

Table 13 showed that a large number of the catalysts tested were found to be unsatisfactory in that the propellant either failed to cure or cured incompletely. In many cases preliminary evidence pointed towards moisture interference. Therefore, a more detailed investigation of the moisture-isocyanate reaction was initiated and is described below.

(1)   General Considerations

The H_2O-RNCO reaction is probably the most important single cause for cure failure. The reaction proceeds via the very unstable carbamic acid, viz

$$RNCO + H_2O \rightarrow [RNHCOOH] \rightarrow RNH_2 + CO_2$$

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which decomposes to amine and CO_2. The amine[*] immediately reacts with a second molecule of isocyanate to form the stable end product, urea. Thus the net reaction is

$$2RNCO + H_2O \rightarrow RNHCONHR + CO_2$$
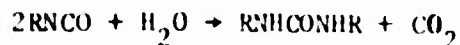
If the water could be quantitatively reacted, the propellant would cure, since only the introduction of additional urea linkages for every molecule of water reacted occurs, e.g.,

$$-CH_2OCONH(CH_2)_6NCO + H_2O + OCN(CH_2)_6NHCOOCH_2-$$

$$-CH_2OCONH(CH_2)_6NHCONH(CH_2)_6NHCOOCH_2-\cdots+CO_2$$
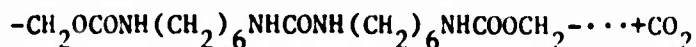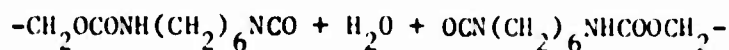
The exact amount of water in a propellant is usually not exactly known. In HTPB binders, moisture poses less of a problem than in polyethers because of the infinitesimal solubility of H_2O in the hydrocarbons. However, as shown above, it takes only minute quantities of H_2O to significantly affect the cure stoichiometry.

(2)   Catalysis of Moisture Reaction

The moisture reaction appears to be catalyzed by the same catalysts which accelerate the urethane reaction. Some metal catalysts, however, are hydrolyzed and are thus inactivated by water. The metal octoates and naphthenates are especially susceptible, while dibutyltin salts appear to be the most stable towards hydrolysis. An indication of catalyst degradation may be the decline of catalytic activity during the course of the reaction. For example, dibutyltin dilaurate is initially less efficient than uranyl acetylacetonate but soon becomes more effective as the reaction proceeds (Figure 12).

---

[*]Aliphatic amines and amines having aromatic skeletons which are not substituted by electronegative groups ($-NO_2$, F) will react much faster than OH with isocyanate. This is in accord with the fact that no free amine is detected in such reactions regardless of the NCO/H_2O ratio. However in amines where the basicity of the NH_2 group is reduced be electronegative substituents, this is no longer the case (16) and chain termination may result.

EFFECT OF CATALYSTS ON THE H_2O-HDI REACTION
(0.2% Catalyst) Acetone Solvent (H_2O=1.1M; HDI=0.23M; T=25°C)
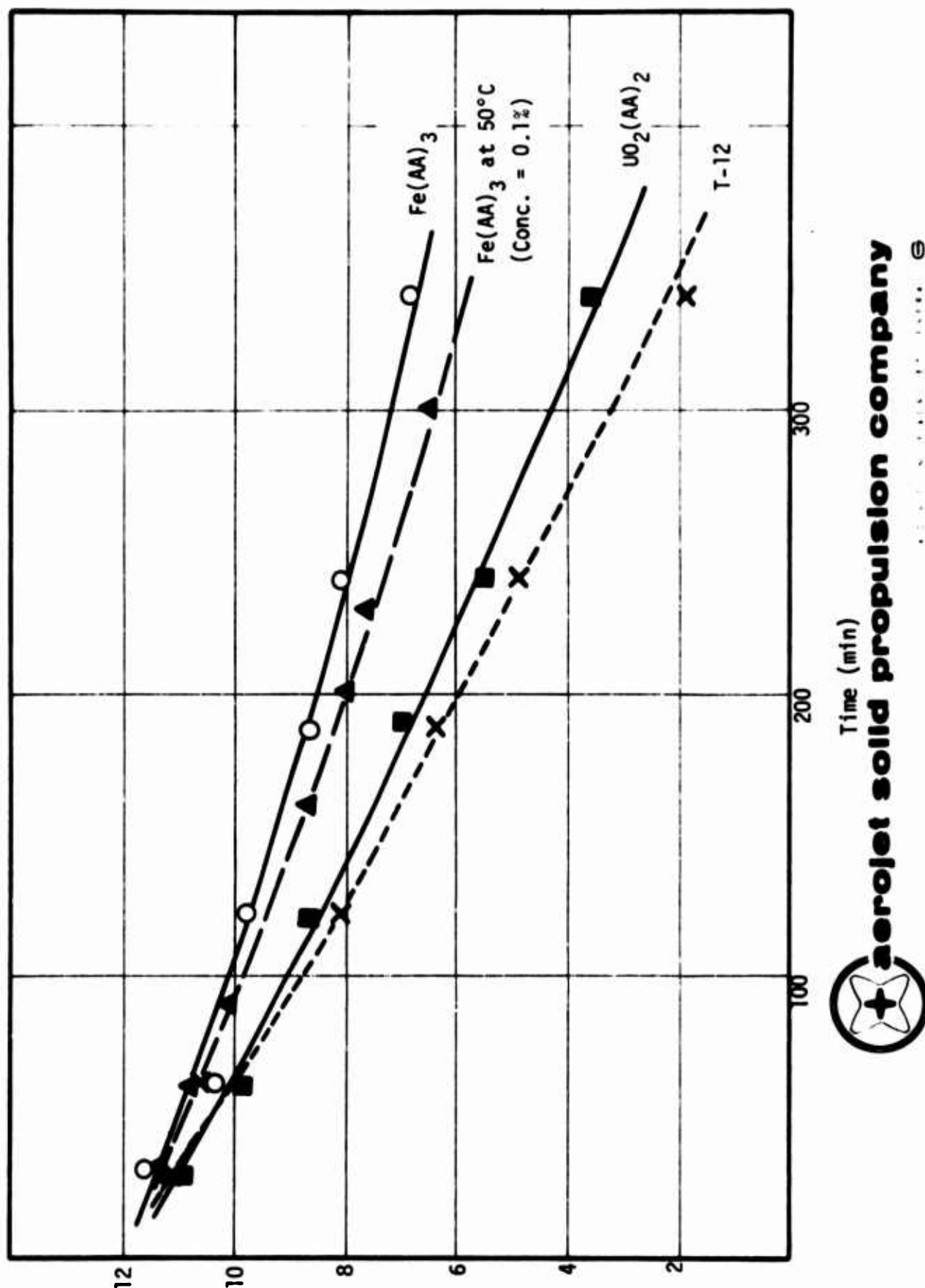
Figure 12

Table 14 lists the relative efficiency of many
metal catalysts for the water reaction with HDI. Acetone was chosen as
solvent, since in dioxane an interference of unknown nature occurs. Because
order and molecularity of the isocyanate-water reaction are unknown, rate data
are listed in terms of percent of the HDI reacted rather than some rate
constant, which depends on the chosen mechanism.

In many instances, the catalyst was not completely
soluble or a precipitate formed as a result of partial hydrolysis by water.
Notably the octoates and naphthenates are susceptible to hydrolysis. Ex-
trapolation of these data to other concentrations and environments are of
questionable value, because of the complexity of the water-NCO reaction.

Since none of the octoates and naphthenates were
completely soluble in acetone containing 2% water, additional studies were
conducted with MEK and ethyl acetate solution which contained only 1% water.
Even here most of the compounds were partially hydrolyzed, evident from the
formation of a precipitate upon the addition of water. The results are shown
in Table 15.

For comparative purposes, the catalyzed isocyanate-
butanol reaction was also studied in acetone at the same molar concentration.
After only 80 min., the reaction was essentially complete with $Fe(AA)_3$ and
dibutyltin dilaurate; with lead naphthenate, lead octoate, and tin octoate,
the reactions were 31, 20 and 25 percent complete, respectively. Comparison
of these results with those in Tables 14 and 15 shows that the urethane
reaction is catalyzed much more effectively than the urea reaction.

Figures 13-16 show time vs. conversion plots for
the uncatalyzed and catalyzed water reaction. Figures 13 and 14 show that
the H_2O-RNCO reaction in the uncatalyzed state is actually faster than the
alcohol-isocyanate reaction for both HDI and TDI at ambient as well as

TABLE 14

RELATIVE EFFICIENCY OF METAL CATALYSTS FOR THE H_2O-HDI
REACTION IN ACETONE[a] AT 25°C

Compound	HDI Reacted[b], %	Compound	HDI Reacted[b], %
Fe(AA)$_3$	38	Cr(AA)$_3$ (i)	10
Mn(AA)$_3$	38	Co(AA)$_3$ (i)	5
Mn(AA)$_2$ (i)	28	Co(AA)$_2$	21
Cu(AA)$_2$ (i)	33	In(AA)$_3$	28
Cu Octoate	71	Ni Octoate (i)	19
Th(AA)$_4$	27	Pb(AA)$_2$ (i)	5
Zr(AA)$_4$	30	Pb Naphthenate (i)	6
Ce(AA)$_4$ (i)	17	Pb Octoate (i)	8
Ce(AA)$_3$ (i)	15	Sn Octoate (i)	19
UO$_2$(AA)$_2$	61	Bu$_2$Sn Laurate	53
V(AA)$_3$	26	Bu$_2$Sn Acetate	75
VO(AA)$_2$	32	Control (24 hrs)	3.5
TiO(AA)$_2$ (i)	28		
Zn(AA)$_2$ (i)	31		
Zn Naphthenate (i)	23		
Zn Decanoate (i)	24		
Ni(AA)$_2$	28		

a H_2O = 1.1M, HDI = 0.23M, catalyst = 0.4%; b HDI reacted (%) in
3 hrs; (i) not completely soluble or partial hydrolysis.

TABLE 15

RELATIVE EFFICIENCY OF SOME METAL CATALYSTS FOR THE WATER - HDI REACTION[a] AT 25°C

	% NCO Reacted During 4 hrs in Solution of	
	MEK	Ethyl acetate
Bu_2Sn Laurate	51	49
Zn Naphthenate (P)	30	14
Zn Decanoate (P)	26	9
Cd Naphthenate (P)	10	9
Cu Octoate	76	68
Sn Octoate (P)	10	5
Pb Octoate (P)	2	1
Pb Naphthenate (P)	2	2

(a) H_2O = 0.55M, HDI = 0.23M; catalyst - 0.4%

(P) Catalyst precipitated upon addition of water.

UNCATALYZED REACTION BETWEEN TDI - BuOH AND TDI - H_2O

BuOH = 1.07M
H_2O = 1.07M
RNCO = 0.5M

BuOH - RT

BuOH - 50°

H_2O RT

H_2O 50°

Time, min

NCO Reacted, mol
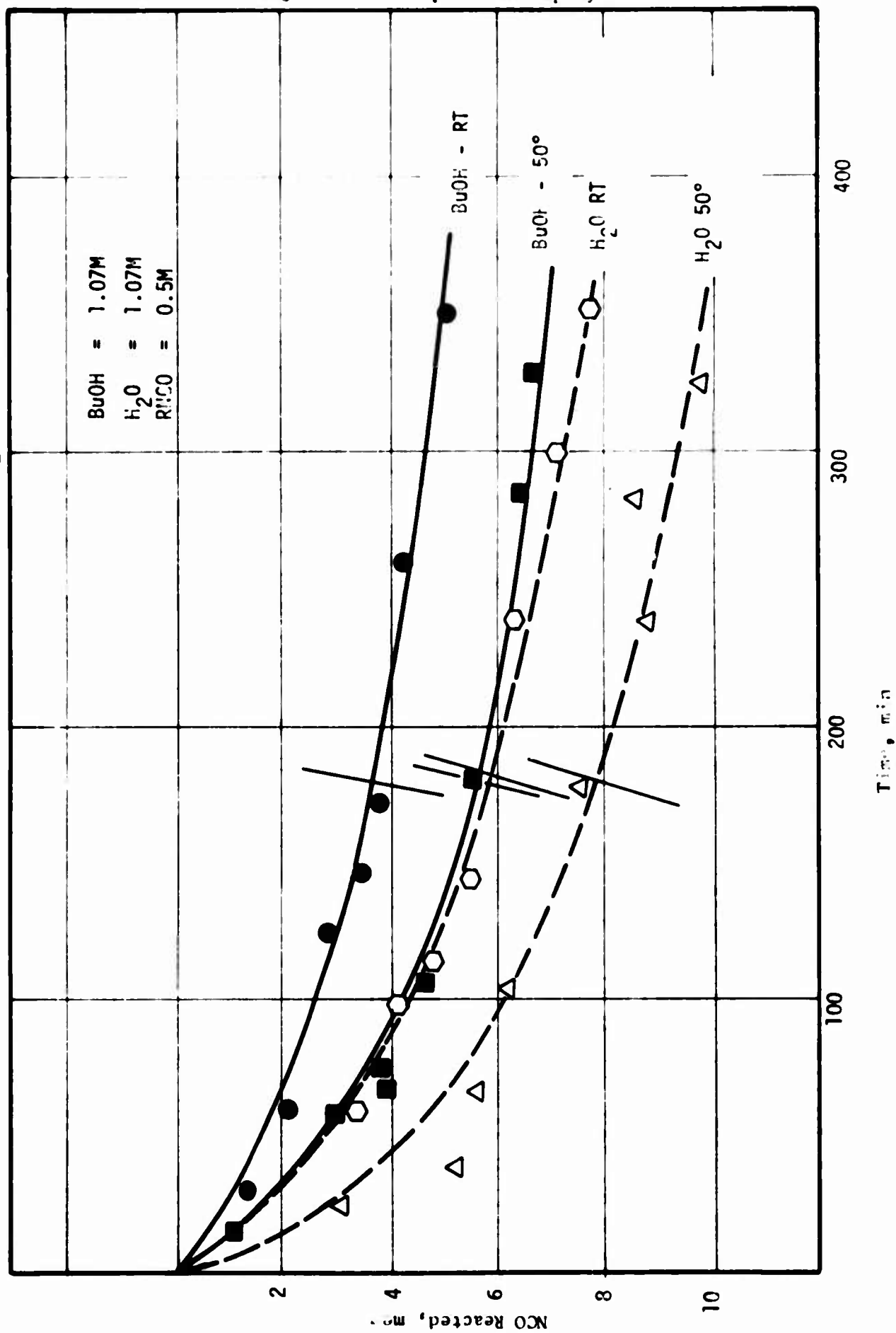
Figure 13

UNCATALYZED REACTION BETWEEN HDI – BuOH AND HDI – H_2O IN ACETONE

BuOH	= 1.07M
H_2O	= 1.07M
RNCO	= 0.5M

BuOH – RT

H_2O – RT

BuOH – 50°

H_2O – 50°

NCO Reacted, meq
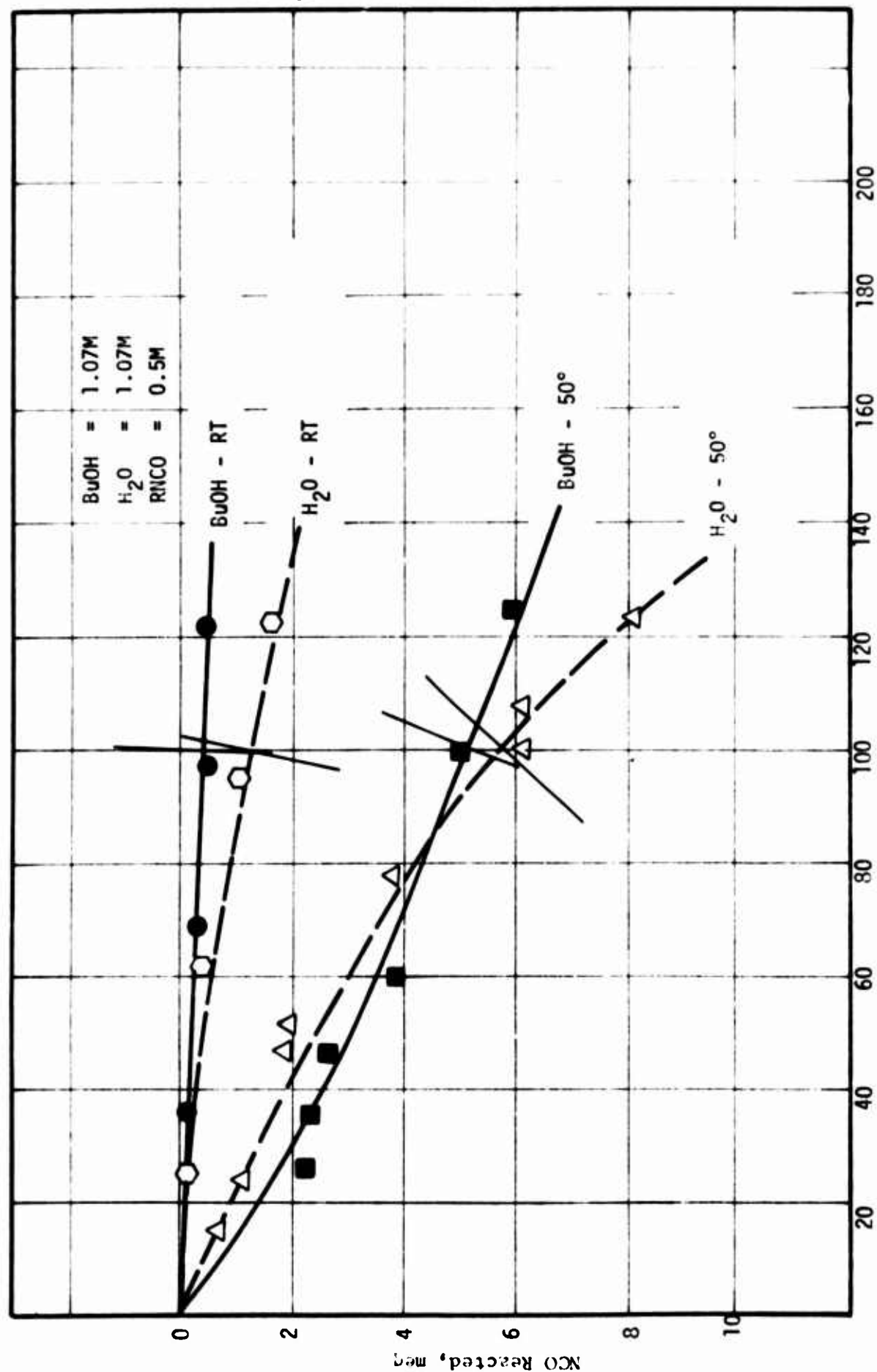
Hours

Figure 14

CATALYZED REACTION BETWEEN HDI AND H_2O IN ACETONE

H_2O = 1.07M
HDI = 0.5M
Cat. = 0.2%

Fe(AA)$_3$ RT

Fe(AA)$_3$ 50°

T-12 RT

T-12 50°

NCO Reacted, meq

Time, min
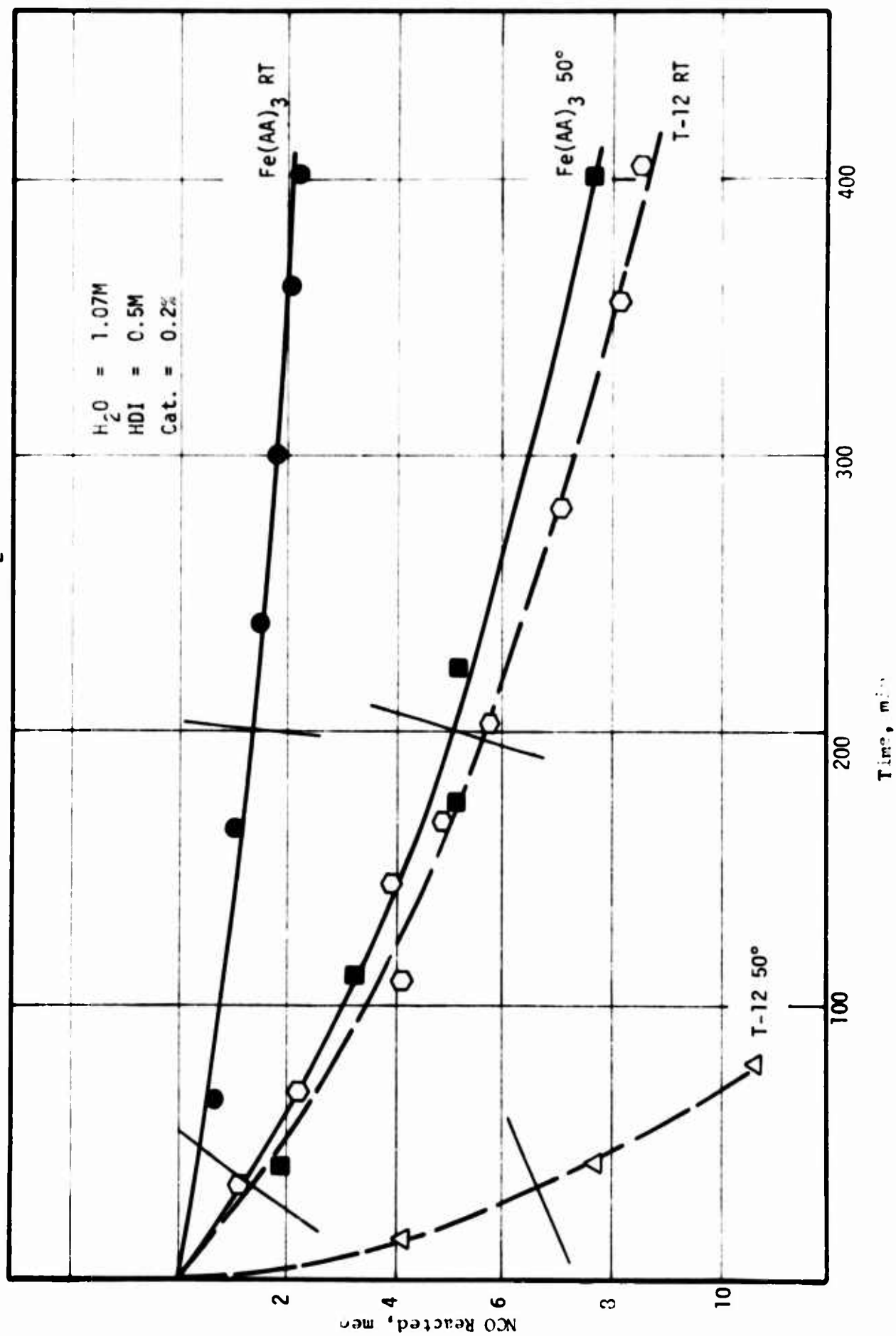
Figure 15

CATALYZED REACTION BETWEEN TDI AND H_2O IN ACETONE

H_2O = 1.07M
TDI = 0.5M
Cat. = 0.2%

Fe(AA)$_3$ RT

Fe(AA)$_3$ 50°

T-12 RT

T-12 50°

Time, min

NCO Reacted, meq
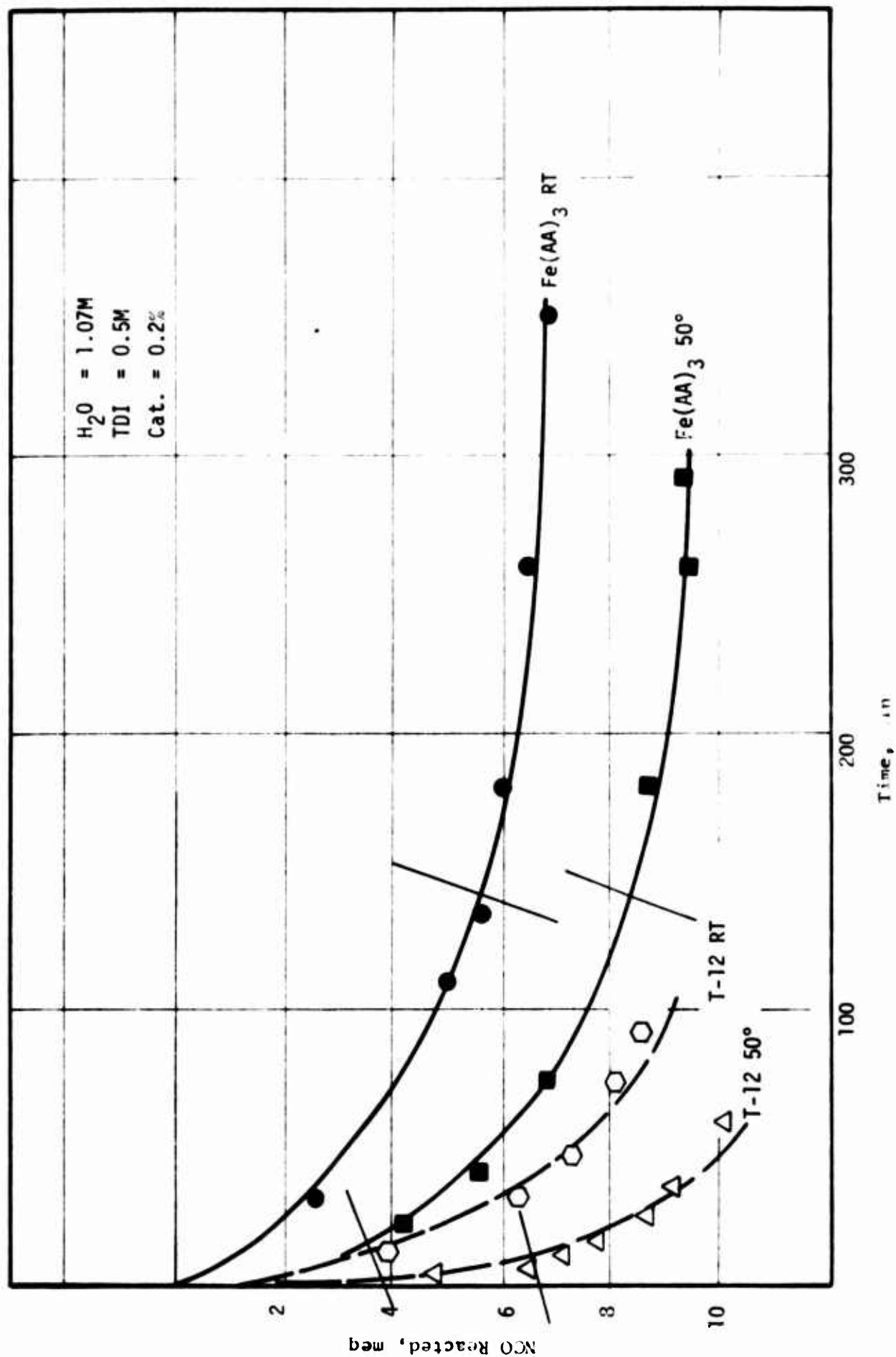
Figure 16

elevated temperature. The effect of temperature on rate is stronger for HDI than TDI reactions, which finds its expression in the much higher activation energy. In order to compare the rates of the H_2O with those of the alcohol isocyanate reactions the apparent second order rate constants were calculated from the graphs. The water-isocyanate reaction is certainly not second order (neither is the urethane reaction), but the first step in the reaction sequence

$$RNCO + H_2O \rightleftharpoons [RNHCOOH] \rightarrow RNH_2 + CO_2$$
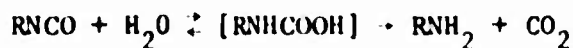
could be second order. Since it is slow compared to the subsequent reaction

$$RNH_2 + RNCO \rightarrow RNHCONHR$$
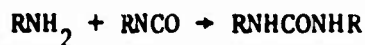
it will be rate determining. The rate constants so obtained depend somewhat on the location of the point on the curve* to which the tangent was drawn. Considering the overall difficulty involved in obtaining these data (Table 16), caution should be exercised in too much extrapolation. Nevertheless it is of interest to compare the rate constants with those found previously for the urethane reaction (cf. Table 7). A PPG/IDP/BuNCO mixture OH=NCO=0.63M, catalyzed with 0.4% T-12 (dibutyltin dilaurate) or $Fe(AA)_3$ respectively, gave 14 and 21 x $10^{-3}E^{-1}min^{-1}$ for the two catalysts at 25°C. A R45/IDP/BuNCO mixture, OH=NCO=0.5M, catalyzed with 0.2% of the tin and iron catalyst, gave 18 and 17 x $10^{-3}E^{-1}min^{-1}$ respectively. Thus it appears that the urethane reaction catalyzed with $Fe(AA)_3$ is about 50 times faster than the H_2O reaction, while this ratio is much less favorable for T-12. Some cure failures observed with T-12 but not with $Fe(AA)_3$, may thus be explained.

---

*In order to obtain comparable values between the reaction velocities at the two temperatures, the rate constants were obtained at the same time. The point at which this was done is indicated by the short line on the curve, which is the normal to the tangent at that point. The normal was drawn by means of a mirror device.

TABLE 16

ACTIVATION ENERGIES AND APPARENT SECOND ORDER RATE CONSTANTS
OF THE REACTIONS SHOWN IN FIGURES 13-16

| | | E(Kcal) [a] | $10^3 k [E^{-1} \ min^{-1}]$ | |
			25°	50°
BuOH/HDI	Uncatalyzed	(12)	0.0043	0.024
BuOH/TDI	Uncatalyzed	5.3	1.3	2.4
H_2O/HDI	Uncatalyzed	(8.5)	0.097	0.27
H_2O/TDI	Uncatalyzed	6.5	2.4	5.5
H_2O/HDI	Fe(AA)$_3$ 0.2%	15	0.35	2.5
H_2O/TDI	Fe(AA)$_3$ 0.2%	3.2	2.9	3.8
H_2O/HDI	T-12 0.2%	20	3.1	44
H_2O/TDI	T-12 0.2%	5.4	29	59

[a]Values in parentheses are less reliable

The activation energies were calculated from the Arrhenius equation

$$k = Ae^{-E/RT}$$

which for the rate constants at two temperatures takes the form

$$\ln(k_1/k_2) = -(E/R)(1/T_1 - 1T_2)$$

Introducing the values for R, T_1 and T_2

$$E = \log(k_2/k_1)/5.7 \times 10^{-5} \text{ cal.}$$

Without knowledge of the true mechanism, it is difficult to define the activation energy of the reaction, thus activation energies calculated here portray essentially only the temperature dependence of the overall reaction. The activation energies calculated from the time-conversion curves shown in Figures 13-16 are listed in Table 16. The values in parentheses are suspect because slow conversion of the uncatalyzed HDI reactions introduces great errors. It is readily observed that temperature changes affect HDI reactions much more than TDI reactions.

It may be mentioned that all rate data concerning the H_2O-RNCO reaction were obtained titrimetrically according to the method described previously. Titrations were conducted electrometrically because of the heterogeneous nature of this reaction and the inherent difficulty in the titration. The polyurea is precipitated during titration as a sticky mass and tends to clog the electrodes. Addition of CCl_4 to the liquid prior to titration alleviates this problem somewhat by forming an emulsion with the polyurea. The reported values have a precision of probably no better than ± 20%. One should also bear in mind that many of the catalysts are decomposed during the reaction which further complicates the picture and makes exact data very difficult to obtain.

In conclusion it may be stated that with respect
to cure failure, water is a most likely culprit. The magnitude of its
effect on cure is lessened with a suitable catalyst,
because the urethane reaction is boosted more efficiently by the catalyst
than the urea reaction. The best catalysts for this purpose appear to be
$Fe(AA)_3$, lead naphthenate, lead octoate and tin octoate. It is not yet
resolved whether poor hydrolytic stability, leading to inactivation of the
catalyst, or truly poor efficiency towards water catalysis is the governing
factor with the latter three.

c.   Homopolymerization of Isocyanates

(1)   Screening of Homopolymerization Catalysts

Another potential side reaction in urethane systems
is isocyanate homopolymerization. The catalyst $Cu(AA)_2$ has been shown to
yield particularly poor propellants if used with HDI cured propellants. A
fast screening test was used to establish catalyst ability to cause homo-
polymerization or selfcondensation reactions of the NCO moiety. For this
purpose the catalysts (50 mg) were stored with pure diisocyanate (10 ml)
for various periods of time. In many cases this quantity of the catalyst
was not completely soluble in the diisocyanate. The results of these tests
are listed in Table 17.

Many of the catalysts caused homopolymerization,
as determined by the formation of gels, precipitates or crystalline species.
Catalysts which did not cause isocyanate homopolymerization under the
conditions of the test were $Fe(AA)_3$, $Bu_2Sn(OOCC_{11}H_{23})_2$, $UO_2(AA)_2$, $Ce(AA)_4$,
$Ce(AA)_3$ and $Co(AA)_3$.

Infrared analysis of NCO homopolymers is difficult
since no characteristic peaks occur. Potassium bromide pellets containing a
variety of glassy homopolymers made with the different catalysts usually
showed a broad peak at 3450 cm^{-1}, the carbonyl band at 1710 cm^{-1} and various
intensities of remaining NCO at 2290.

TABLE 17

CATALYZED HOMOPOLYMERIZATION OF DIISOCYANATES
(10 ml isocyanate, 50 mg catalyst)

Catalyst	HDI			TDI		
	2 days RT	4 hrs, 140°F	2 days, 140°F	4 hrs RT	5 days RT	2 days, 140°F
Pb Naphthenate	G*	-	-	SG	G	-
$Cu(AA)_2$	G	-	-	OK	OK	OK
Sn Octoate	G	-	-	G	-	-
$Zn(AA)_2$	G	-	-	nt	nt	nt
$Ni(AA)_2$	OK	G	-	OK	OK	OK
$Mn(AA)_3$	OK	G	-	SG	SG	SG
$In(AA)_3$	OK	G	-	P	P	C
Ni Octoate	OK	G	-	OK	OK	OK
Zn Decanoate	OK	G	-	OK	SG	SG
$Mn(AA)_2$	OK	G	-	P	P	C
$Co(AA)_2$	OK	OK	G	OK	OK	OK
$(Bu_2SnO)_x$	OK	OK	G	OK	G	-
$VO(AA)_2$	OK	dl	G	OK	dl	dl
Cu Octoate	OK	OK	G	nt	nt	nt
Bu_3SnCl	OK	-	G	nt	nt	nt
$TiO(AA)_2$	OK	dl	G	dl	dl	dl
$V(AA)_3$	OK	dl	G	OK	dl	dl
$Th(AA)_4$	OK	OK	G	nt	nt	nt
$Fe(AA)_3$	OK	OK	OK	OK	OK	OK
$Bu_2Sn(OOCC_{11}H_{23})_2$	OK	OK	OK	OK	OK	OK
$UO_2(AA)_2$	OK	OK	OK	OK	OK	OK
$Zr(AA)_4$	OK	OK	OK	nt	nt	nt
$Bu_2Sn(OAc)_2$	OK	OK	OK	nt	nt	nt
$Po(AA)_2$	OK	OK	OK	P	P	SG
Pb Octoate	OK	OK	OK	SG	G	-
$Cd(AA)_2$	OK	OK	OK	P	P	P
$Ce(AA)_4$	OK	OK	OK	OK	OK	OK
$Ce(AA)_3$	OK	OK	OK	OK	OK	OK
$MoO_2(AA)_2$	OK	OK	OK	OK	OK	OK
$Co(AA)_3$	OK	OK	OK	OK	OK	OK
Cd Naphthenate	OK	OK	OK	P	P	P
$Ca(AA)_2$	OK	OK	OK	nt	nt	nt
$Mg(AA)_2$	OK	OK	OK	nt	nt	nt
$Zr(AA)_4$	OK	OK	OK	OK	OK	G

G = hard gel, SG = soft gel, P = precipitate, C = crystallized, dl = dark liquid, nt = not tested

(2) Mechanism of NCO Selfcondensation

The mechanism of NCO homopolymerization is not clearly understood. However, it is known that some metal chelates, particularly $Mn(AA)_3$ are powerful catalysts for vinyl polymerization. Bamford and Ferrar[17] propose a mechanism as follows:
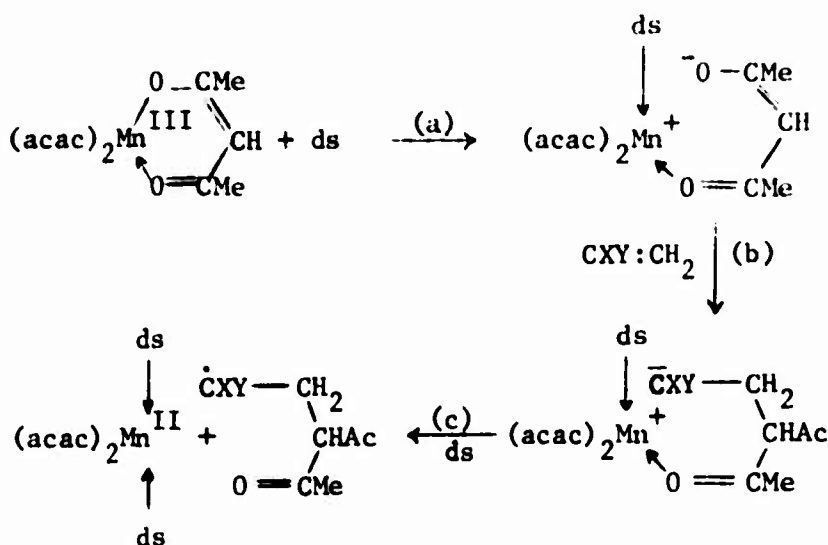
where ds denotes an electron donor, e.g. an ether or amine group. Whether such a mechanism is responsible for NCO homopolymerization is not clear, but since the double bond in styrene is certainly less reactive than the double bonds in an isocyanate group, it is not improbable that classes of compounds which catalyze vinyl polymerization will cause polymerization of NCO groups.

(3) Effect on Cure

Selfcondensation of isocyanates may be the second most important cause of cure failure particularly in HTPB propellants where moisture interference, due to the infinitesimal solubility of water, is a less likely cause. A number of the more promising catalysts from the

previous screening program were tested in a R45/IDP/TDI binder system loaded to 85 percent with AP and aluminum. In this test propellant, the necessary crosslink level can be adjusted by simply varying the concentration of the diisocyanate because the functionality of the HTPB system is greater than two. The effect of TDI variations in such a system is shown below.

| TDI wt% | Mechanical Properties at +77°F | | |
	σ_m, psi	ϵ_m, %	E_o, psi
0.42	90	30	370
0.46	172	20	1100
0.50	194	14	1730

$\overline{\dot{\epsilon}} = 0.74$ in./in./min.

A TDI level of 0.44% and a catalyst level of 0.005% was chosen. The catalysts tested included $Fe(AA)_3$ (control), lead naphthenate, nickel octoate and copper octoate. With the exception of the dibutyltin dilaurate and the $Fe(AA)_3$ control, none of the catalysts gave satisfactory cure. All appeared to be deficient in isocyanate and yielded soft, undercured propellants.

The fact that T-12 yielded rather hard propellants indicates that water interference was not the cause of cure failure. Infrared studies on the benzene extract* of the uncured propellant showed no NCO absorption, therefore incomplete reaction can be ruled out. In fact addition of more TDI brings about cure in all the propellants with all catalysts tested to date. While this correction of cure is possible in the case of R45 type

*To obtain the benzene extract a quantity of the uncured propellant is digested with benzene. Solids are allowed to settle and the clear supernatant layer is decanted into an evaporating dish. Most of the benzene is evaporated in a vacuum over. From the concentrated solution a smear is prepared whose IR spectrum is immediately obtained. Figure 19b shows such a spectrum.

HTPB propellants, it may not be so in systems with more difunctional pre-
polymers. Therefore it is important to gain more insight into the mechanism
of this type of cure interference. This cure failure is most probably caused
by homopolymerization of isocyanate.

(4) Types of Self Condensation Reactions

Self condensation reactions of isocyanates can
yield a variety of products, the most probable and well known ones being
dimers, trimers and linear polymers, viz:

dimer   trimer   linear polymer
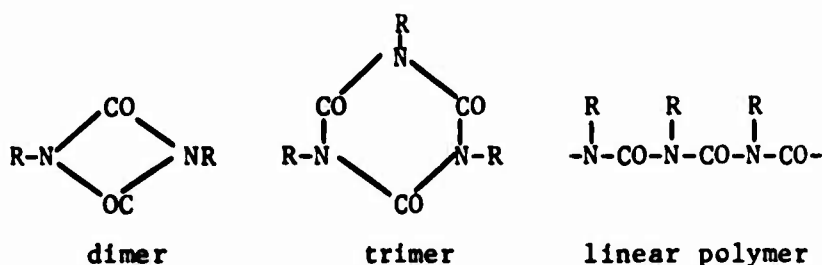
At high temperatures and with suitable catalysts, condensation to carbodiimides
(R-N=C=N-R) may occur from the previously obtained dimer. Dimerization of
aliphatic isocyanates is not known.

If dimerization and trimerization occur it is
obvious that it may lead to cure failures due to NCO deficiency. For example,
in case of dimer formation, four equivalents of NCO are required to react
and link together two equivalents of OH. Thus for every dimer linkage formed
two unconnected chains remain, i.e., in effect we obtain chain termination, if
a stoichiometric NCO/OH ratio was used initially. In the case of the trimer,
one effective crosslink is formed from three equivalents of NCO, if the NCO
groups stem from prepolymer chains, whose OH groups have reacted with a di-
isocyanate. Again, three OH groups must of necessity remain unreacted yield-
ing three unconnected chain ends. As far as network formation is concerned

one unreacted chain end just about neutralizes one trifunctional crosslink, so that the net effect of trimerization as well as dimerization is the reduction of the crosslink level, provided that the diisocyanate was not used in excess.

In the linear homopolymer every reacting NCO group produces a branch point and one residual OH group. Thus crosslinking and chain scission neutralize each other. But since urethane formation is in almost all cases considerably faster than selfpolymerization, and because of a statistical distribution of the reacted species, there will be totally unreacted diols (serving as inert diluents in the network), and the net effect will be a very highly branched but very weak binder matrix. The type of condensation reaction occurring in the binder matrix should therefore be reflected in the mechanical properties of the cured product, as will be shown later.

(5) Catalysts for Selfcondensation Reactions

HDI and TDI selfcondensations in toluene (10% solution) were conducted in sealed ampules. The content of the ampules were inspected periodically for evidence of gelation and/or precipitate. The results essentially corroborate those obtained earlier (Table 17). The catalysts which did not cause either precipitation or gelation of TDI during 7 days ambient temperature storage followed by 2 days at 180° were Fe(AA)$_3$, iron III hexafluoroacetylacetonate, dibutyltin dilaurate, MoO$_2$(AA)$_2$, Th(AA)$_4$, Zr(AA)$_4$, Cr(AA)$_3$, and Co(AA)$_3$. Gels were produced by lead octoate, lead naphthenate and tin octoate. All other catalysts yielded variable quantities of an insoluble precipitate. TiO(AA)$_2$, V(AA)$_3$ and VO(AA)$_2$ formed intensively dark solutions. In case of the HDI-toluene solution, gelation was effected by lead naphthenate, lead octoate, Cu(AA)$_2$, copper octoate, tin octoate, In(AA)$_3$, V(AA)$_3$, VO(AA)$_2$ and zinc naphthenate. The latter four produced a gel only after the 180° storage. No marked change was found with Fe(AA)$_3$,

dibutyltin dilaurate, $UO_2(AA)_2$, $Zr(AA)_4$, $Cr(AA)_3$ and $Co(AA)_3$. As with TDI $TiO(AA)_2$, $V(AA)_3$ and $VO(AA)_2$ formed very dark solutions.

Butyl isocyanate and phenyl isocyanate were also subjected to homopolymerization reactions, because, being monomeric compounds, they yield well defined condensation products, and thus shed light on the products of homopolymerization brought about by the metal catalysts. In this case only the more potent catalysts for selfcondensation; namely, tin octoate, lead octoate and naphthenate, copper octoate and $Cu(AA)_2$ were tested with phenyl isocyanate and butyl isocyanate. The products of the condensation were found to be practically pure trimer. $Fe(AA)_3$ and T-12 were used as controls and again proved rather ineffective in producing trimerization, as were the copper compounds in case of the phenyl isocyanate. The products were identified by melting point, NMR, infrared and molecular weight determinations. The tributyl cyanurate is a high boiling liquid. Thus it appears that these catalysts promote essentially trimerization reaction. Only in the case of the copper compounds and aliphatic isocyanates formation of some linear polymer may occur as indicated by a rather insoluble fraction and a molecular weight somewhat higher than that corresponding to the trimer. In the infrared spectrum of trimerized phenyl isocyanate (Figure 17A) the peak at 3400 cm^{-1} is difficult to explain, since in that region either OH or NH stretching frequencies are involved. This grouping should not be present in homopolymerized isocyanate. A literature[18] article claims that some urea groups which could explain this peak are formed in the homopolymerization of TDI.

Figure 18A shows the infrared spectrum of the HDI homopolymer from $Cu(AA)_2$ in TEGDME, and Figure 18B the TDI homopolymer resulting from the addition of stannous octoate to pure TDI. The spectra are of little analytical value, because of the absence of characteristic peaks. For comparative purposes the infrared spectrum of a polyurea made from HDI and

PHENYL ISOCYANATE TRIMER FROM ∅NCO + Sn OCTOATE

Structure
Corroborated
by NMR

Figure 17A

INFRARED SPECTRA OF POLYUREA

Figure 17B

(-NHCONH(CH$_2$)$_6$-)$_n$

Double Peak of Urea
Carbonyl

-77-
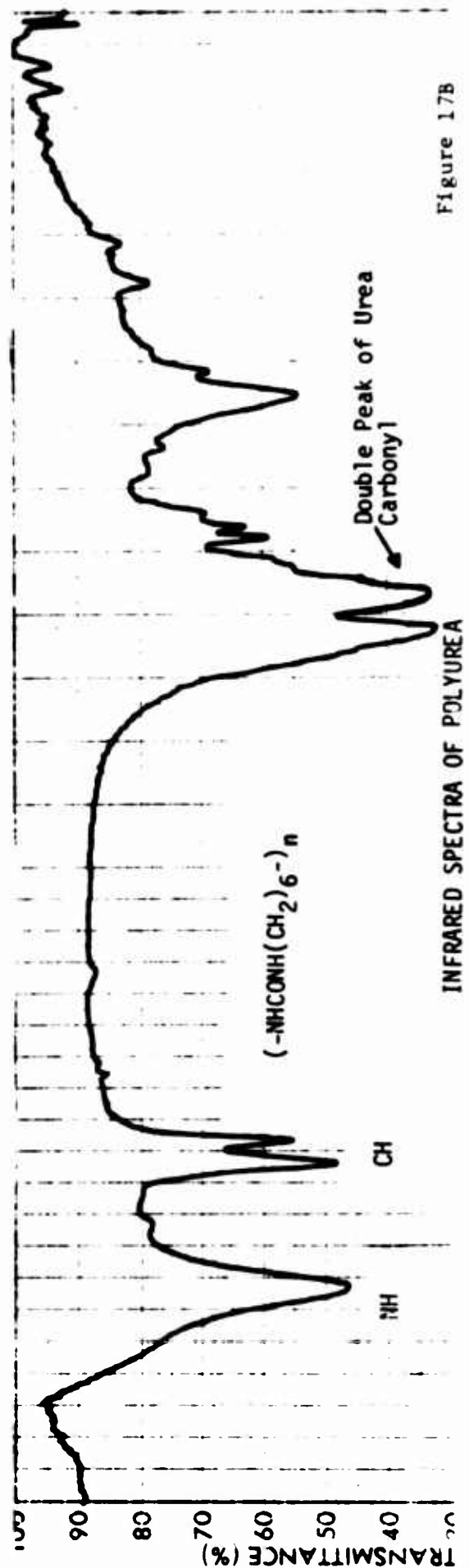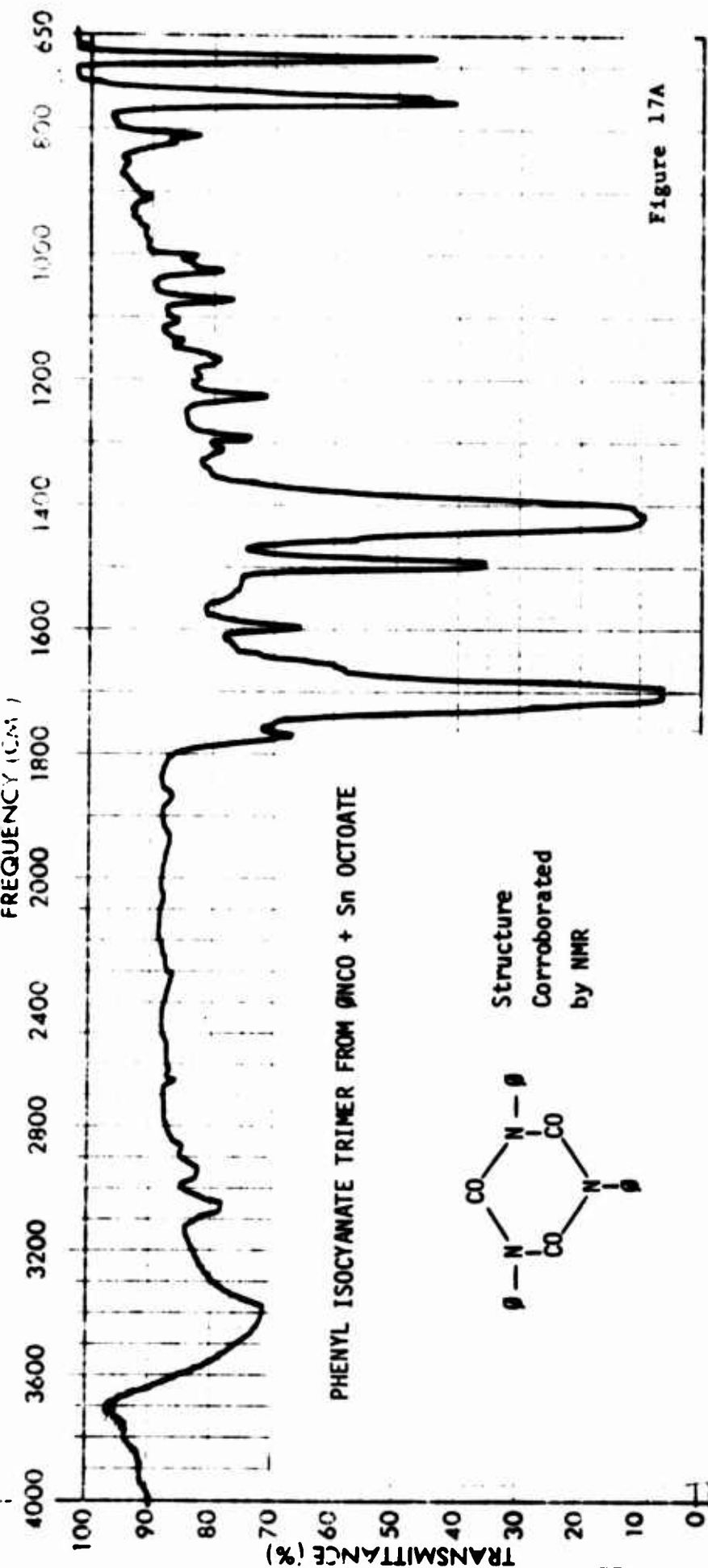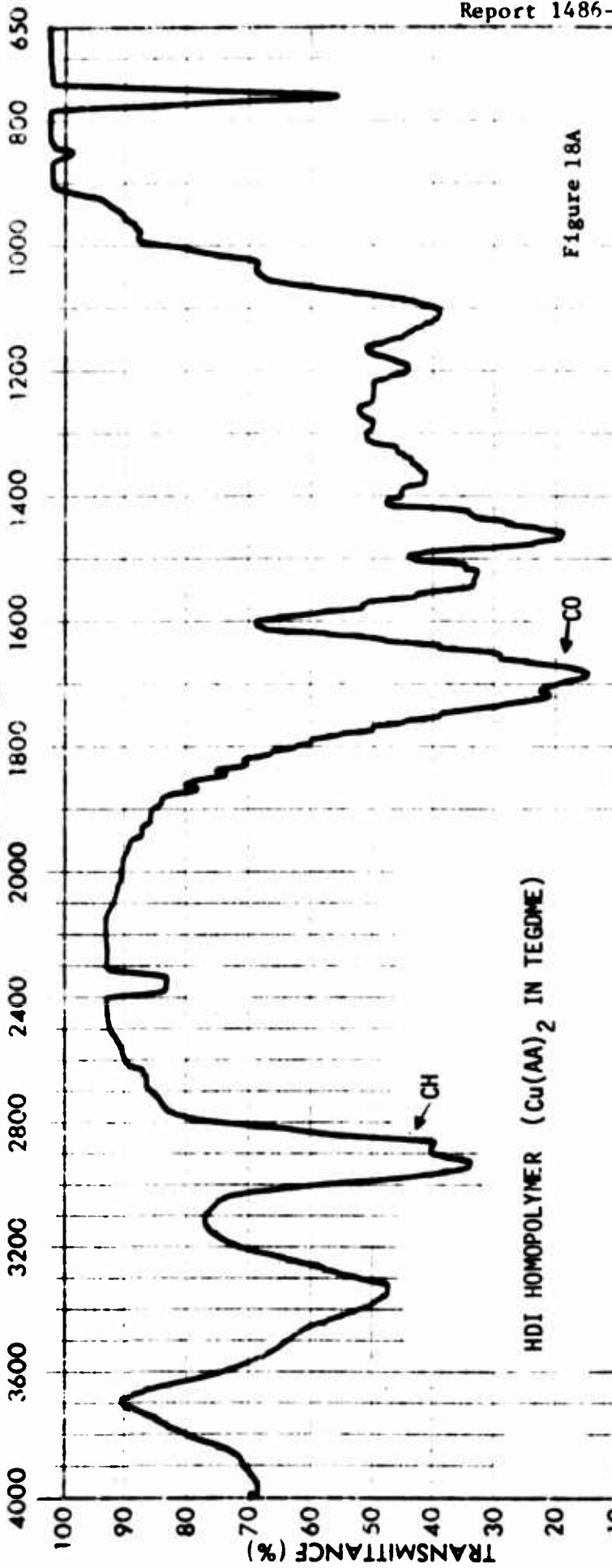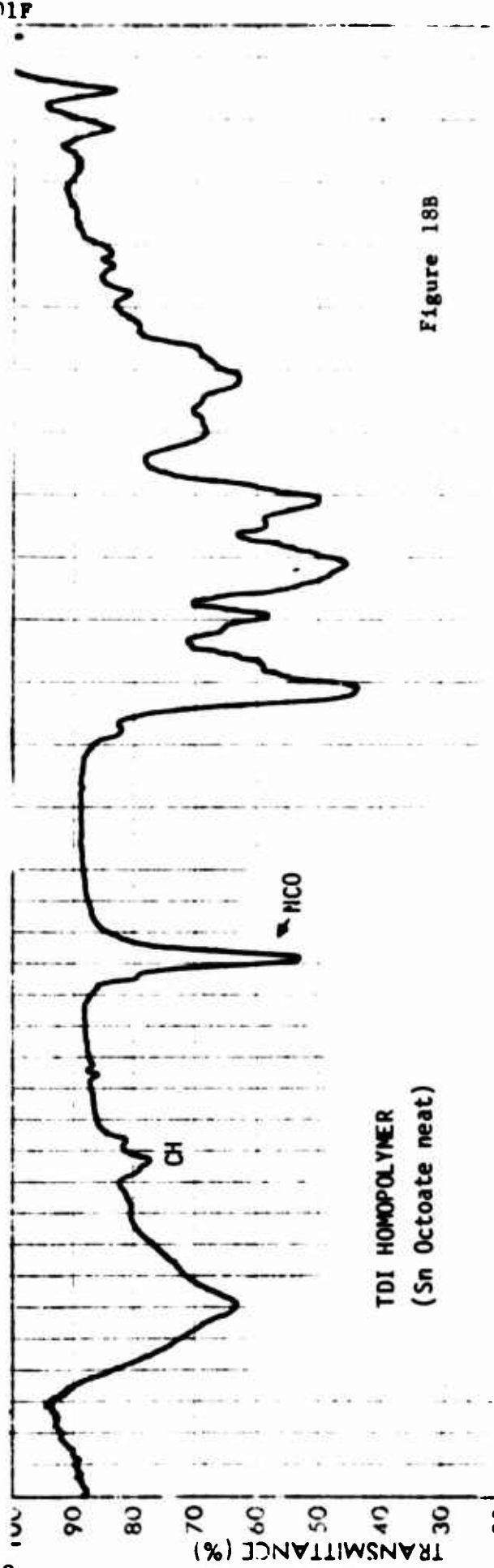
INFRARED SPECTRA OF ISOCYANATE HOMOPOLYMERS

water is shown in Figure 17B. The absence of the double peak of the urea
carbonyl (Figure 17B) rules out the suspicion, that the HDI homopolymer may
be mainly the result of an accidental H_2O-HDI reaction. The most important
infrared absorption bands are summarized in Table 18 (from Ref. 18).
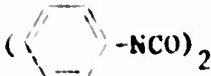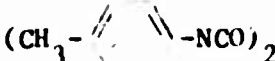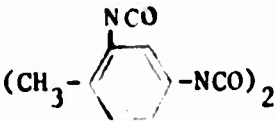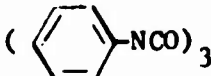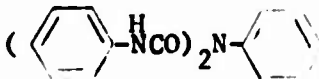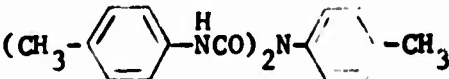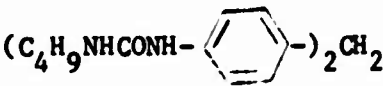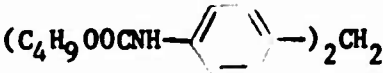
It is interesting to note that $Cu(AA)_2$, which is
very active in bringing about homopolymerization of HDI appears to be much
less effective towards TDI. Homopolymerization is also effected by non-
metallic compounds. Tertiary amines, both aromatic and aliphatic, are well
known, but also some ethers, particularly tetrahydrofuran, were found in this
study to cause gelation of TDI. Solvents can augment the metal catalyzed
homopolymerization very effectively. In some tests those compounds containing
electron donor atoms (ether oxygen and tertiary nitrogen) are quite syner-
gistic. For example, addition of lead naphthenate to a 10% solution of TDI
in dioxane or dimethylformamide caused a very strong exotherm. The TDI
solution containing lead naphthenate gelled within three days at ambient
temperature in the following solvents: ligroin, cyclohexane, carbon tetra-
chloride, dioxane and dimethylformamide. MEK and butyl acetate solutions
remained liquid, at least, during the first 10 days at room temperature.
Thus it may be anticipated that the backbone structure of the prepolymers
and plasticizers used in propellants will affect the cure reaction.

(6) Investigation of Trimerization as
Crosslinking Reaction

The trimerization leading to cure may be depicted
as follows:

TABLE 18

INFRARED ABSORPTION SPECTRA OF MODEL COMPOUNDS IN KBr PELLETS

Compound	I R Bands, cm^{-1}				

A. Dimers

| | 1780(s)[a,b] | 1608(s) | 1507(s) | 1421(us) | |

| | 1785(ms)[b] | 1622(ms) | 1515(s) | 1387(s) | |

| | 2270(m)[c] | 1775(m)[b] | 1622(m) | 1496(m) | 1387(s) |

B. Trimers

| | 1780(m) | 1708(s)[b] | 1631(ms) | 1496(ms) | 1414(s) |

| | 1775(wm) | 1710(s)[b] | 1622(m) | 1518(ms) | 1408(s) |

C. Biurets

| | 1714(s)[b] | 1675(m) | 1594(ms) | 1530(s) | 1446(s) |
| | 1315(m) | 1262(m) | 1225(m) | 1182(m) | |

| | 1714(s)[b] | 1665(m) | 1594(ms) | 1514(s) | 1403(m) |
| | 1310(m) | 1262(m) | 1228(m) | 1178(m) | 1168(m) |

D. Urea

| | 1642(s)[b] | 1594(m) | 1550(m) | 1515(m) | 1411(wm) |
| | | | 1308(m) | 1234(m) | |

E. Urethane

| | 1698(s)[b] | 1616(m) | 1530(s) | 1416(m) | 1340(m) |
| | | | 1311(m) | 1230(s) | |

(a) Intensities are designated qualitatively: w, wm, m, ms, s, us.
(b) Carbonyl stretching frequency.
(c) Isocyanate group.

$$3 \ ROCONH(CH_2)_6NCO \rightarrow$$
$$I$$
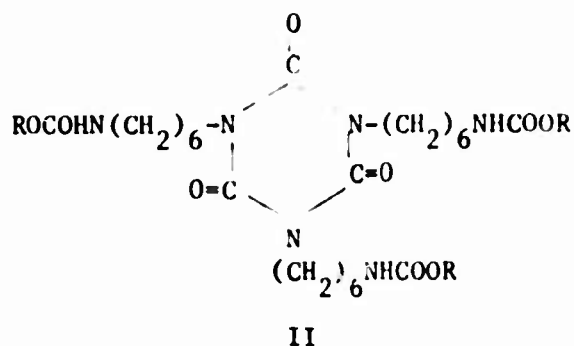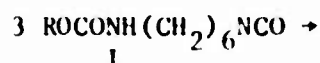
where I denotes a prepolymer molecule reacted with hexamethylene diisocyanate. In order to obtain one crosslink three NCO terminated prepolymer molecules have to be converted into the cyanurate ring II. The additional NCO needed to obtain the necessary crosslink density, ν_{tb}, can be estimated from Equation 10. Thus for a crosslink density of 5×10^{-5} moles branch points per gram of rubber, with no other crosslinker being used, the weight fraction of trimer (of HDI) is given by:

$$W_1 = 3 \times 84 \times 5 \times 10^{-5} = 1.26 \times 10^{-2}$$

Hence 1.26% HDI is required over the amount necessary for the urethane reaction to produce the necessary crosslinking in the binder phase. For a typical propellant this quantity would reduce to about 0.1 to 0.2 percent, since propellants usually contain no more than 10-20% binder.

Table 19 shows some of the test results. About the same levels of isocyanate are needed if the B-2000 prepolymer is replaced by HTPB or other suitable prepolymers. Because of the obvious advantages that such a cure system offers (i.e., no separate crosslinker is required) more work was devoted to the exploration of homopolymerization.

TABLE 19

CURE OF B-2000 WITH EXCESS TDI OR HDI USING
SELFCONDENSATION CATALYSTS
CURE 24 HRS AT 160°F

TDI Eq %	Sn Octoate (0.5%)	Pb Naphthenate (0.5%)
103	No cure	No cure
115	No cure	Soft cure
126	Cure	Cure
137	Cure	Cure
150	Cure	Cure

HDI Eq %	Sn Octoate (0.5%)	Pb Naphthenate (0.5%)	$Cu(AA)_2$ (0.5%)
83	No cure	No cure	No cure
95	No cure	No cure	Soft cure
107	No cure	No cure	Cure
119	Cure	Cure	Cure
131	Cure	Cure	Cure
143	Cure	Cure	Cure
155	Cure	Cure	Cure

Lead naphthenate is best suited for TDI homo-
polymerization while $Cu(AA)_2$ is the most potent catalyst for HDI. Pro-
perties of binders prepared with B-2000 and excess HDI or TDI are compared
in Table 20.

The mechanical properties obtained with the B-2000/
HDI/$Cu(AA)_2$ binders are extremely poor and the B-2000/TDI/Pb naphthenate
binders are not much better. In both systems unconnected chain ends and an
inherently high crosslink density seem to be responsible. More experimen-
tation showed that only $Cu(AA)_2$ or copper octoate produced cures in the
presence of AP. All other catalysts failed in the presence of AP.

Table 21 lists a number of solids which were
tried in the TDI/B-2000 binder containing 30 equivalent percent excess TDI.
The homopolymerization catalyst was either 0.2% lead naphthenate or tin
octoate. Ammonium compounds were found to inhibit homopolymerization by
the above two catalysts as indicated in the table, while HDI selfconden-
sation, initiated by $Cu(AA)_2$, is not greatly affected by the ammonium salts.
The reason for this difference between $Cu(AA)_2$ and the divalent lead or tin
compounds is not known, but may perhaps lie in the coordination between the
metal ion and the isocyanate group. In the copper-isocyanate complex
attachment of Cu^{2+} is probably to the N atom of the NCO moiety (since Cu
forms strong amine complexes) while in the lead and tin compounds association
is more likely through the oxygen atom of the NCO group, because amine
complexes of the latter two metals are weak. This hypothesis would also
explain the particular efficiency of $Cu(AA)_2$ with HDI (HDI has a more basic
N atom than TDI), while it is not so active toward TDI homopolymerization.
The two activated complexes may perhaps look as follows:

$$
\begin{array}{cc}
\begin{array}{c}
(+) \\
R-N=C=O> \\
\downarrow \\
Cu^{2+}
\end{array}
&
\begin{array}{c}
R-\underline{N}=C=\overline{O} \rightarrow Pb^{2+} \\
(+)
\end{array}
\\
\\
I & II
\end{array}
$$
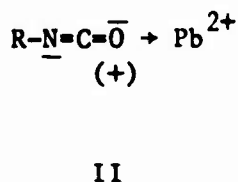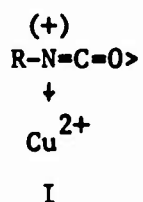
TABLE 20

20a   MECHANICAL PROPERTIES OF B-2000/EXCESS HDI BINDER CATALYST
0.05% $Cu(AA)_2$

Eq. % HDI	σ_m, psi	ϵ_m, %	E_o, psi
96	21	220	18
107	31	100	57
117	47	64	144
128	48	37	222

20b   MECHANICAL PROPERTIES OF B-2000/EXCESS TDI BINDER CATALYST
0.3% LEAD NAPHTHENATE

Eq. % TDI	σ_m, psi	ϵ_m, %	E_o, psi
126	55	280	48
137	80	210	96
149	138	160	130

TABLE 21

EFFECT OF VARIOUS SOLIDS (80% b.w.) ON CURE OF B-2000/TDI (130 Eq. %)

Catalyst either lead naphthenate or tin octoate at 0.2% each.

Solid	Cure after indicated days at	
	160°F	Ambient
NH_4ClO_4	Neg 3	Neg 5
Glass beads	Pos 1	Pos 2
$KClO_4$	Pos 1	Pos 2
LiF	Pos 1	Pos 2
$NH_4H_2PO_4$	Neg 3	Neg 10
NH_4Cl	Neg 3	Neg 10
NH_4Br	Neg 3	Neg 10
$(NH_4)_2C_2O_4$	Neg 1	Neg 10
NH_4BF_4	Neg 1	Neg 10
$MgSO_4$	Pos 1	Pos 3
MgO	Pos 1	Pos 3
$CaHPO_4$	Pos 1	Pos 3
$CaSO_4$	Pos 1	Pos 3
AlF_3	Pos 1	Pos 3
$MnCl_2$	Pos 1	Pos 3

Obviously the two complexes will undergo different mechan'sms of homopoly-
merization. The nitrogen atom is electrophilic in I, and nucleophilic in
II. The quite different properties obtained from the two types of catalysts
could perhaps be due to this difference. In addition, in structure I the
N atom will repel protons (stemming from the ammonium salt) which may block
the N atom for further reactions, while this is not so in structure II,
where hydrogen bonding to the nitrogen is not impaired. Thus the inhibition
of homopolymerization by ammonium perchlorate in the case of Pb^{2+} or Sn^{2+}
catalyzed systems may be explained.

Attempts to overcome this inhibition of trimeri-
zation by addition of basic substances like dimethylaniline, pyridine or MgO
in practical quantities (up to 1%) failed to re-establish cure, and infrared
spectra of uncured batches showed the presence of unreacted NCO.

Further investigations were therefore concentrated
on the $HDI-Cu(AA)_2$ combinations which is not affected by ammonium salts. A
concentration series showed that within the range of 0.002 to 1% $Cu(AA)_2$
about the same state of cure was obtained. The properties of such propellants
are extremely poor as shown in Table 22.

The next approach was to use a dual catalyst system
in which one catalyst was an efficient urethane catalyst ($Fe(AA)_3$ or dibutyl-
tin dilaurate) i.e., a compound which was ineffective towards homopolymeri-
zation and the second catalyst was $Cu(AA)_2$ to trimerize residual NCO groups.
Surprisingly, the urethane catalyst inhibited trimerization, or if trimeri-
zation was affected by large quantities of $Cu(AA)_2$ or high temperature, the
resulting propellant properties was no better than those achieved with $Cu(AA)_2$
alone. Figure 19 shows the infrared spectrum of a propellant extract in
which an $Fe(AA)_3-Cu(AA)_2$ combination was employed. For comparison, the I.R.
spectrum of the pure binder phase employing only the urethane catalyst (in
the latter case the binder does not cure because of NCO termination) is shown.

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TABLE 22

TRIMERIZATION CROSSLINKED B2000/IDP/HDI PROPELLANTS
(65% AP, 15 Al) CATALYZED BY $Cu(AA)_2$. CURED 5 DAYS AT
ROOM TEMPERATURE

HDI, Eq.%	Mechanical Properties at +77°F[*]		
	σ_m, psi	ε, %	E_o, psi
100	31	34	140
110	50	30	280
120	68	18	620
130	68	17	680
140	70	15	735

[*]$\dot{\varepsilon}$ = 0.74 in./in./min

B-2000/HDI COMBINATION CONTAINING 140 EQ. % HDI AFTER COMPLETION OF
URETHANE REACTION IN (A) PURE BINDER PHASE AND
(B) PROPELLANT

-88-

Figure 19
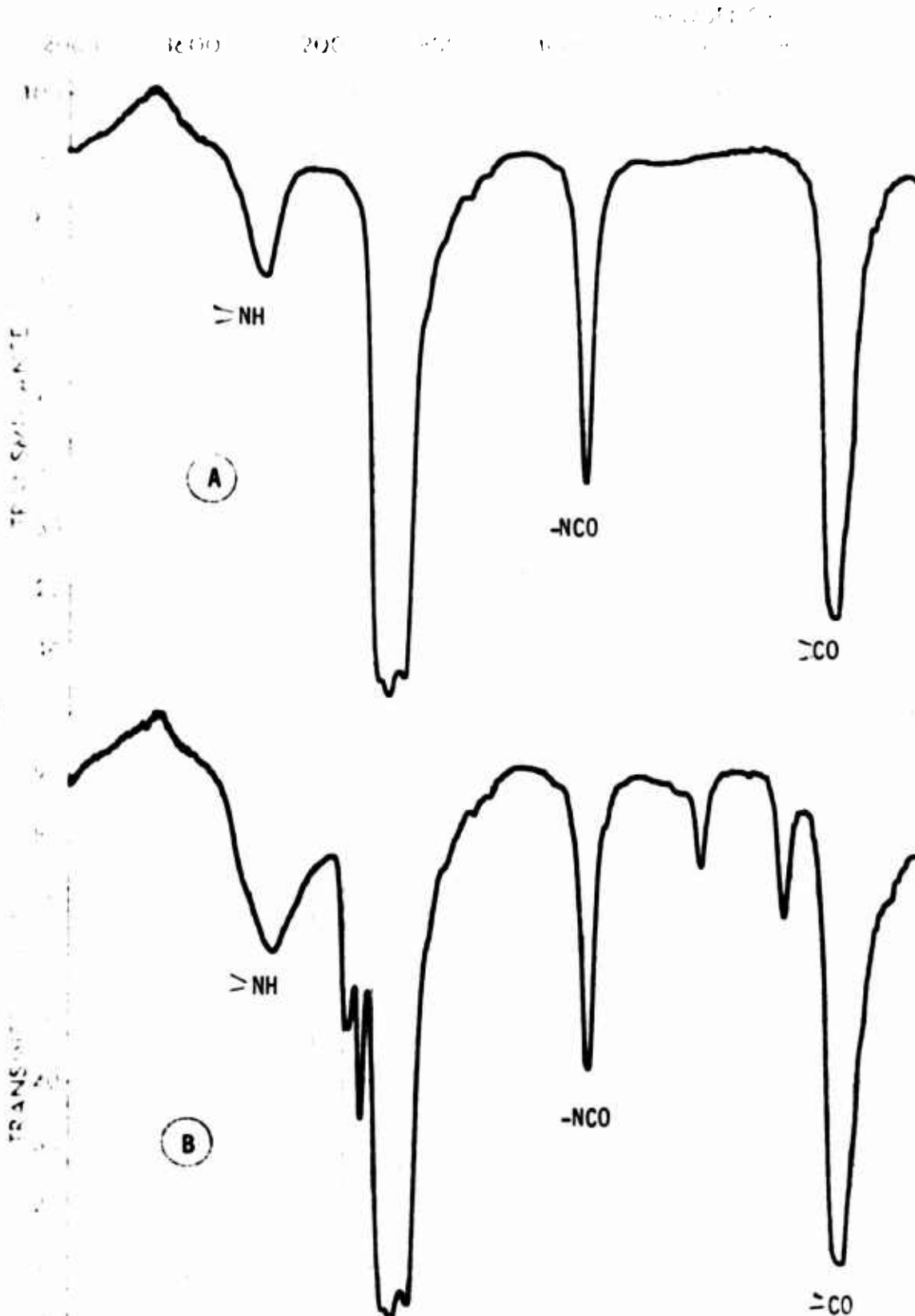
This interference with $Cu(AA)_2$ effected homopolymerization reactions was shown by all the catalysts tested and was independent of the presence of AP. The other catalysts tested in combination with $Cu(AA)_2$ were dibutyltin dilaurate, $Mn(AA)_3$, $Th(AA)_4$, $UO_2(AA)_2$, $Zn(AA)_2$, tin octoate, lead octoate and $MoO_2(AA)_2$. Again, the reason for this behavior is not clear. One hint may be the observation that free acetylacetone also inhibits the homopolymerization reaction. Thus HAA liberated from the urethane catalyst may block the action of $Cu(AA)_2$. This explanation is, however, highly conjectural.

To summarize, the poor properties of propellants containing a binder matrix crosslinked through trimerization, preclude application in practical propellants.

d. Other Contaminants

(1) The Effect of Ammonium Perchlorate on Cure

Figure 20 shows the effect of 0.5 percent of dissolved AP in PPG* on the rate of the urethane reaction. The tests were conducted on stoichiometric PPG-BuNCO mixtures catalyzed by 0.01% $Fe(AA)_3$. The extent of reaction was ascertained with a Beckman I.R. 9 spectrophotometer by periodic measurement of the intensity of the carbonyl band indicating formation of the urethane link. Apparent second order constants calculated from the slopes after 10 minutes reaction are 1.6×10^{-2} E^{-1} min^{-1} for the PPG-BuNCO mixture containing the dissolved AP and 2.3×10^{-2} E^{-1} min^{-1} for the control. Thus AP definitely affects the rate of cure. This has also been observed qualitatively in that urethane propellants always cure slower than unfilled binders.

---

*Of presently used prepolymers only PPG dissolves enough AP (0.5% of AP in dry PPG at room temperature) to study the effects of the salt on cure and rate of cure in homogeneous solution.

EFFECT OF 0.5% DISSOLVED AP ON THE RATE OF CONVERSION
IN THE PPG-BuNCO REACTION CATALYZED WITH 0.01%
$Fe(AA)_3$ AT ROOM TEMPERATURE

$k_{2(AP)} = 1.6 \times 10^{-2} \text{ L}^{-1} \text{ min}^{-1}$

$k_{2(control)} = 2.3 \times 10^{-2} \text{ L}^{-1} \text{ min}^{-1}$

PPG/AP

PPG Control

Time, Minutes

BuNCO Consumed, Eq. x 10^2
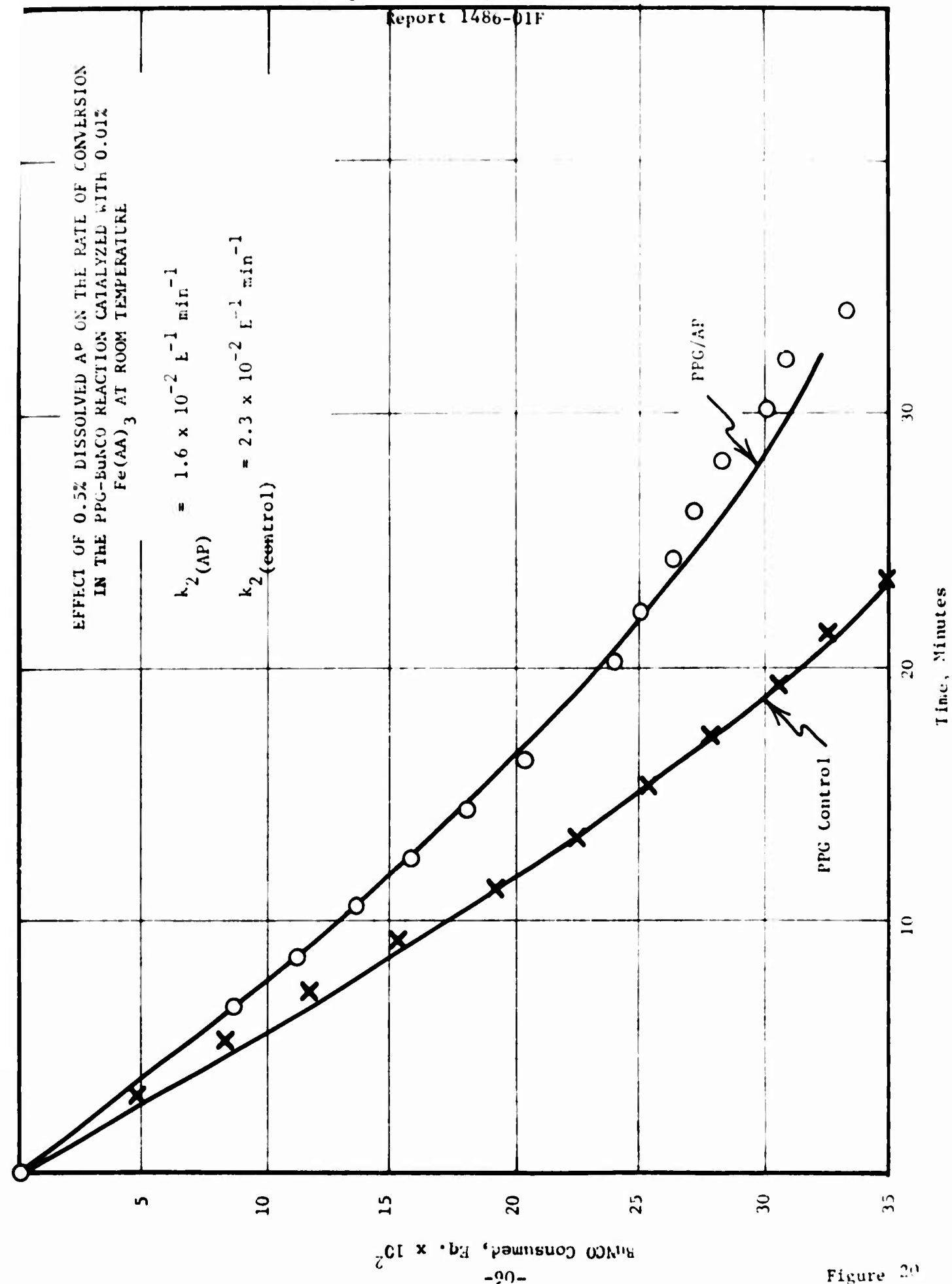
Figure 29

In Tables 23 and 24 the effects of AP and various catalysts on isocyanates are shown for several conditions of storage. In these tests a 10% solution of either HDI or TDI in dry toluene was added to AP to yield a mixture containing 80% b.w. AP and 20% solution. This approximates roughly the amount of AP to which the isocyanate in a propellant binder will be exposed. Catalysts were tested at a nominal concentration of 0.05%. The mixture was contained in Erlenmeyer flasks fitted with well greased glass stoppers to positively prevent admittance of moisture. The flasks were stored either at room temperature or 150°F for various lengths of time. Prior to testing the contents of the flasks were diluted 4:1 with toluene and the intensity of the NCO band was compared with that of the stock solution from which the samples were made. In the uncatalyzed stock solution both HDI and TDI were found to be stable, i.e., no detectable reduction of the NCO band was observed. The precision of the tests was about ± 5% as judged from duplicate runs.

The data in Tables 23 and 24 indicate that well dried AP, in general, does not consume isocyanate. In fact, since it inhibits the hu polymerization brought about by some of the catalysts, the concentration of unreacted NCO is often greater in the presence of AP.

Table 25 shows the effect of ambient vs 150°F storage on the stability of HDI-toluene solution containing some representative catalysts.

(2) Effect of Impurities on Catalyst Activity

The cure catalysts developed were also tested in the presence of impurities such as HF, HCN, H_2O, $HClO_4$, HNO_3, NO and NO_2. With the exception of HF, and possibly HCN none of the above impurities inactivates the iron catalysts but they will, in large concentration, seriously impair the cure by reaction with the isocyanate group. A short discussion of each of the impurities follows.

TABLE 23

EFFECT OF AP[a] AND VARIOUS CATALYSTS ON TDI SELF-CONDENSATION. 20 HRS 150°F.

Catalyst	Per Cent of the TDI Left in[b]	
	10% Toluene Solution	80% AP + 20% Toluene Sol.
None	100	100
$Fe(AA)_3$	97	97
$Bu_2Sn(OOCC_{11}H_{23})_2$	89	90
Pb Octoate	79	91
Pb Naphthenate	63	88
Sn Octoate	88	89
Sn Naphthenate	89	86
$Cu(AA)_2$	78	84
$UO_2(AA)_2$	91	91
$TiO(AA)_2$	82	88
$Th(AA)_4$	89	89
$VO(AA)_2$	79	77

[a]Unground and dried 4 days at 250°F in air.

[b]The concentration of TDI in the toluene stock solution immediately after preparation is taken to be 100%.

TABLE 24

EFFECT OF AP[a] AND VARIOUS CATALYSTS ON HDI SELF-
CONDENSATION.   STORAGE 20 HRS AT 150°F.

Catalyst	Per Cent of the HDI Left in	
	10% Toluene Solution	80% AP + 20% Toluene Sol.
None	99	98
$Fe(AA)_3$	98	95
$Bu_2 Sn(OOCC_{11}H_{23})_2$	91	89
Pb Octoate	88	84
Pb Naphthenate	0[b]	79
$Cu(AA)_2$	0[b]	71
Sn Octoate	60	73
Zn Decanoate	80	82
$TiO(AA)_2$	64	73
$Zr(AA)_4$	78	81
$UO_2(AA)_2$	77	83
$MoO_2(AA)_2$	95	(73)
$Th(AA)_4$	83	84
$V(AA)_3$	73	77
$Mn(AA)_3$	80	80
$In(AA)_3$	80	87
Sn Oleate	60	not tested
Sn Laurate	73	not tested
Sn Naphthenate	55	not tested

[a] Dried 4 days at 250°F.

[b] All HDI had gelled. Gel was not soluble in toluene and its free NCO
content was not determined.

TABLE 25

EFFECTS OF CATALYSTS ON HDI SELFCONDENSATION DURING STORAGE FOR 3 DAYS AT AMBIENT AND 150°F

No NH_4ClO_4 Present

Catalyst	HDI (% of Original) After 3 Days Storage at	
	Ambient	150°F
None	100	99
$Fe(AA)_3$	97	96
Bu_2 Sn Laurate	85	85
Sn Octoate	85	50
Pb Naphthenate	83	0^a
Pb Octoate	93	61
$Cu(AA)_2$	0^a	0^a

[a] HDI had gelled.

For these tests propellants were formulated with
the R-45M-HDI binder system containing 85 wt% solids (70% AP and 15% Al). In
some propellants where the aluminum was omitted, the solids content was
80% by weight. The R-45M binder was chosen because the propellant will cure
even if the catalyst is destroyed, provided the impurity in question does
not greatly interfere with the urethane reaction. From the hardness of the
cured propellants conclusions were drawn as to whether the impurity in
question has affected cure stoichiometry.

(a) HF

Almost all metal ions which are catalytical-
ly active in urethane catalysis are transformed into inactive insoluble
fluorides by HF and thus lose their catalytic efficiency. This includes such
metals as Fe, Mn, Th, Pb, Co Ni and Zn. Soluble fluorides are formed by the
metals Sn, Ti, Zr, V and Mo. Mixed chelate salt type compounds still
possessing catalytic activity will initially be formed. However, if the con-
centration of HF becomes too high, even these metals will eventually be
converted into undissociated ineffective complexes of the type SnF_6^-, TiF_6^-,
etc. Thus the most promising approach appears to be a good scavenger for HF.

To investigate the effects of HF on propellant
cures, $NaHF_2$ was added to the mix at 2 and 5% level, replacing an equal amount
of oxidizer. This concentration of sodium bifluoride converts the $Fe(AA)_3$
(used at the 0.01% level) into white, inactive FeF_3 within approximately
4 hours. In order to retard cure, 0.01% of HAA was also added, otherwise the
propellant would cure within one hour at this high level of catalyst before
the HF could effect catalytic activity.

$Fe(F_3AA)_3$ and $Fe(\emptyset_2AA)_3$ were also converted
to inactive FeF_3 in about the same time as $Fe(AA)_3$. The decomposition of the

catalysts is readily observed in nonaluminized propellants, where the
initial pink color stemming from the dissolved iron chelate fades to white.
The propellant containing the $NaHF_2$ then continues to cure like the un-
catalyzed control. Propellants containing the bifluoride cured slightly
softer than controls not containing the bifluoride, indicating only minor
interference of HF with the urethane reaction. $Zn(AA)_2$ and dialkyltin
salts (like dibutyltin dilaurate) appear to work best in the presence of
HF, although their activity is also strongly reduced. In other tests, metal
oxides ZnO, PbO, MgO, Al_2O_3 were evaluated as scavengers for HF. Of these,
only ZnO provided an improvement in cure.

Binder soluble salts like lithium stearate
calcium palmitate and calcium stearate were tested and found to give minor
improvements in the cure.

Following a suggestion of C. S. Kim, several
epoxides were tested because an epoxide readily undergoes ring opening with HF

$$R-\underset{\underset{O}{\diagdown\diagup}}{CH-CH}_2 + HF \rightarrow R\underset{\underset{OH}{|}}{CH}-CH_2F$$
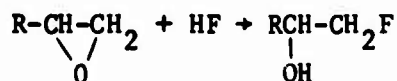
However, these additives did not provide significant improvement of catalyst
stability.

(b) $HClO_4$

Perchloric acid was added to the propellant
at the 0.01% level in the form of the dihydrate (70% $HClO_4$). Water free
perchloric acid cannot be tested in these systems, since violent explosion
occurs on contact with organic matter. Catalytic activity was not signifi-
cantly affected and the test propellant cured normally. In order to study
the effect of acids on cure, nonaluminized propellants were used to avoid
loss of the acid due to reaction with the metal. Iron chelates form mixed

complexes with acids, e.g., $Fe(AA)_2ClO_4$. These compounds, as well as $Fe(ClO_4)_3$, are practically as active as the $Fe(AA)_3$ so that even if all the iron is converted into $Fe(ClO_4)_3$, it still performs as a catalyst because it is soluble in organic media. Caution must also be exercised during experimentation with dilute $HClO_4$.

(c) HNO_3

Since highly concentrated HNO_3 (90%) ignites spontaneously on contact with R-45M, the usual concentrated (70%) acid was used in these experiments. Propellants containing up to 0.1% of this acid cured satisfactorily. Like perchloric acid, nitric acid forms catalytically active mixed salt-chelate type iron compounds which are also effective catalysts.

(d) NH_3

Ammonia is a very common impurity in AP propellants. It is usually liberated through reaction of basic bonding agents such as alkanolamines or polyamines with ammonium perchlorate. During the interim vacuum mix cycle, much of this ammonia is removed and that which remains is instantaneously reacted upon addition of isocyanate. As long as there is free isocyanate (i.e. incomplete cure) the concentration of ammonia in a propellant is negligible. If large quantities of NH_3 are evolved during cure, the stoichiometry of the cure reaction may be sufficiently disturbed to lead to cure failure, whether or not the catalyst has been affected by the ammonia.

(e) NO, NO_2 and HCN

The effects of the gases NO, NO_2, and HCN on catalyst activity were tested as follows:

A three liter flask containing 10 ml of a 1% Fe(AA)$_3$ solution in dibutyl phthalate was evacuated and then filled with the gas in question. After 4 days of ambient storage the efficiency of the catalyst was tested using the exotherm method described before. The results are listed below in terms of a relative reaction rate based on the activity of the untreated Fe(AA)$_3$ solution:

Gas	Relative Rate
None	1
NO	0.96
NO$_2$	1.29
HCN	0.15

Of the three gases only NO was inert towards Fe(AA)$_3$. The solution treated with NO$_2$ was completely bleached and the Fe(AA)$_3$ was probably converted into Fe(NO$_3$)$_3$. Ferric salts (if soluble) can be catalytically more active than Fe(AA)$_3$ which could account for the increased rate of this sample. Although the Fe(AA)$_3$ solution exposed to HCN did not visibly change, the efficiency of the catalyst was strongly reduced. At present it is not known whether another, less dissociated iron complex, perhaps Fe(AA)$_2$CN or the like has formed.

After discussion of the study of impurities with Dr. J. Trout, it was decided to deemphasize further work on the effect of these impurities.

3. Effect of Duration of Cure on Propellant Reproducibility

The cause for the softer cure of slow curing propellants is usually attributed to the higher extent of NCO consuming side reactions. As will be shown later there is good reason for this assumption because

catalysis accelerates the urethane reaction more than side reactions, so
that the ratio of desirable to undesirable reactions becomes more favorable.
In turn if these side reactions were somehow suppressed, it is believed,
that the mechanical properties of a slow curing and a fast curing propellant,
ultimately should be the same, provided they reach the same state of cure,
i.e., the same extent of reaction. This assumption, which is based on the
present theory of elasticity, appears to be incorrect. According to this
theory, such properties as modulus, tensile strength and equilibrium swelling
are determined by the number of elastically effective chains per unit volume
of rubber, "while their length is of secondary importance only".[15] Thus,
the distribution of chain lengths which is affected by variations in cure
rate, is not considered a significant parameter of rubber networks. This
distribution of chain length, however, was found experimentally to be quite
a significant factor, and that it is affected by the rate of cure becomes
plausible if we contemplate what catalysis does to the individual binder
species used in the usual propellant binders. Normally these contain triol
and diol type prepolymers. Assume that we have a binder mixture containing
a small quantity (10-20 equivalents) of a slowly reacting triol (e.g. a
polyether) the remainder being a fast reacting diol (e.g., HTPB prepolymer),
and the diisocyanate. A good catalyst will boost the reactivity of the slow
hydroxyl groups to almost that of the fast hydroxyl groups, so that we can
expect the crosslinker to be randomly interspersed between the molecules of
the diol. In poorly catalyzed binders the diol will react much faster than
the crosslinker which may, under certain conditions, lead to comparatively
long chains and bunching of crosslinks. According to present theory, however,
the two binders should be identical or nearly so, since they both possess
the same number of chains, and differ only in the distribution of chain
lengths, which as stated previously is not thought to be significant. In
propellant cure tests described later, it was observed that the only slightly
catalyzed and therefore very slowly curing propellants invariably cured much

softer than the fast curing propellants. However, the great length of time
during which these slowly curing HTPB propellants were gaining modulus and
tensile strength made the presence of NCO consuming side reactions question-
able. Thus it was decided to investigate whether nonrandom chain length
distribution could be responsible for the effect of softer cure. The premise
was tested in the following way: Binder specimens were prepared which had
exactly the same composition but differed in the way they were made.
Table 26 shows some examples with B-2000 type elastomers. In the first four,
B-2000 was prereacted with HDI in various proportions to yield longer hydroxyl
terminated chains. This corresponds to the case where the diol reacts more
rapidly than the triol. To this long diol the TP-4040 and the remainder of
HDI was added and binder cure was completed in the usual manner. Table 26
also contains the equilibrium benzene swelling and the crosslink density
values calculated from the Flory-Rehner equation (23) using a μ factor of
0.3. This factor may not be entirely correct for this elastomer-solvent
combination, but a wrong interaction parameter does not greatly affect the
relative values of crosslink density so obtained, which is
important for this comparison. Obviously the elastomer which should have
the longest chains (or widest distribution of chain lengths) swells most
and consequently appears to possess lowest crosslink density. In
fact, all five binders should have the same crosslink density since they
differ only in the sequence in which the prepolymers were reacted, the amount
of crosslinker being identical.

An argument against the validity of this experiment is
that the effects of chain termination[14] are multiplied if prereaction is
carried out on diols whose functionality is less than two. This is shown
in Table 27 for Binders 4 and 5 where chain termination was deliberately
introduced. Table 27 contains a similar series of elastomers using the
combination of PPG with TP-2540. PPG is practically difunctional and
there is less danger of building long monofunctional or nonfunctional

TABLE 26

EFFECT OF CHAIN LENGTH DISTRIBUTION ON MECHANICAL PROPERTIES

OF POLYURETHANE RUBBERS MADE FROM B-2000[a] AND TP-2540[b] WITH HDI

Composition: TP-2540 25.5%, B-2000 65.9%, HDI 8.3%
Neozone D 0.2%, $Fe(AA)_3$ 0.1%

Composition of Prereacted Component, Equivalents			Uniaxial Tensile Properties @ 77°F				$v_e \cdot 10^4$ Moles Chains per cm³
B-2000	HDI	EW	σ_m, psi	ϵ_m, %	E_o, psi	v_2	
5	4	5136	64	133	84	0.121	0.99
4	3	4092	59	112	88	0.128	1.09
3	2	3048	67	97	110	0.139	1.27
2	1	2004	75	95	120	0.144	1.38
1	-	960	84	101	140	0.153	1.55

(a) Poly(1,2-oxybutylene)diol MW 2000

(b) Poly(1,2-oxypropylene)triol MW 2550

TABLE 27

EFFECT OF CHAIN LENGTHS DISTRIBUTION ON MECHANICAL PROPERTIES

AND CROSSLINK DENSITY OF PPG ELASTOMERS[a]

Rubber No.	Procedure	Unaxial Tensile Properties @ 77°F	v_2	$v_e \cdot 10^4$
1	All ingredients present simultaneously	70/76/165	.156	1.62
2	3 moles PPG prereacted with 2 moles HDI	74/86/159	.149	1.50
3	6 moles PPG prereacted with 5 moles HDI	67/105/120	.133	1.17
4	3 moles PPG prereacted with 2 moles HDI and 1/2 mole BuNCO	22/180/24	.115	0.87
5	TP-2540 prereacted with 1/2 mole BuNCO	63/254/69	.101	0.67
6	All ingredients present simultaneously	106/310/85	.119	0.95

[a]Composition of elastomers: TP-2540 1 mole, PPG 3 moles, HDI 4.5 moles, Neozone D 0.2% and Fe(AA)$_3$ 0.1%. In Rubbers 4 and 5, 0.25 moles HDI are replaced by 1/2 mole butyl isocyanate, and in Rubber 6 only 1/2 mole of the crosslinker TP-2540 is used per 3 moles PPG and 3.75 moles HDI.

chains, than with the less well-defined B-2000. Again it
is apparent that the rubber in which all components were reacted simultaneously
appears to be the most highly crosslinked of the six. Rubber 2 does not
differ markedly from it, because the composition of this rubber is such
that the average chain length between crosslinks corresponds roughly to the
3/2 prepolymer*. If however six moles PPG are reacted with five moles HDI,
prepolymer chains result which are markedly longer (roughly twice as long)
than the average chain length obtained in Binder 1. Accordingly its equilib-
rium swelling and mechanical properties appear to be those of a less highly
crosslinked rubber. Binders 4 and 5 demonstrate the effects of chain
termination. In Binder 4 the long chain diol is terminated with butyl
isocyanate resulting in a rubber where about 70% of the network consists of
ineffective nonload bearing chains, while in Rubber 5 only about 15% of the
network consists of dangling chain ends, which is reflected in the must better
properties of Rubber 5. The best properties are obtained if crosslink density
is reduced by decreasing the weight fraction of the triol rather than by chain
termination, for which Rubber 6 is an example.

Finally Table 28 shows the same effect of prereaction for the
HTPB prepolymer Lot 242AM-310. Because of the inherently high MW of this
prepolymer only two chains were hooked together with HDI**. This results in
an average EW of 4964 for the prereacted chain (the EW of 242AM-310 is 2440).
The same quantity of crosslinker (1 equivalent crosslinker per equivalent
original diol) again yields a much softer material for the rubber having the
longer chains.

---

* The theoretical crosslink density $\nu_{th} = W_c/2E_c = 1.72 \times 10^{-4}$ (moles chains/cm^3),
where W_c is the weight fraction of crosslinker and E_c is the equivalent weight.
Hence $M_c = 1/\nu_{th} = 5800$. The 3/2 prepolymer has an EW of 2870 and the 6/5 pre-
polymer an EW 5820. Note $EW_{PPG} = 900$; $EW_{TP2540} = 850$ and $EW_{HDI} = 84$. The density
of these rubbers are practically unity. 3/2 designates the equivalence ratio
PPG/HDI of the prereacted diol.

**Higher extents of prereaction lead to unmanageably high viscosities.

TABLE 28

EFFECT OF PREREACTION ON MECHANICAL PROPERTIES AND EQUILIBRIUM SWELLING IN HTPB RUBBERS

(HTPB Lot 242AM310)

Composition, g		Uniaxial Tensile Properties			v_2
Prereacted diol		86	194	129	0.123
GTRO	74.46				
HDI	10.50				
	3.78				
Neoz D	0.2c				
FeAA	0.01				
As received diol		91	117	177	0.151
GTRO	73.20				
HDI	10.50				
	5.04				
Neoz D	0.20				
FeAA	0.01				

All examples show that rubbers with a wider distribution of
chain lengths, i.e., containing the longer chains, will be softer and swell
more, than rubbers with a more narrow distribution (i.e. shorter chains),
although the total number of chains is the same. Such long chains have
been produced by prereacting the diol components. This technique is applic-
able to these prepolymers, because transesterification (as in polyester)
leading to randomization does not take place in the urethane linkage or, at
least, is very slow at ordinary temperatures.

If the prepolymer functionality is lower than two, selective
reaction can lead to even more softening, due to formation of long mono-
functional chains which leads to a high weight fraction of dangling ends
that are mechanically ineffective (cf Rubber 4 in Table 27).

In HTPB binders the diol component is usually of significantly
higher reactivity than a polyether crosslinker and if it is also the major
component with respect to its contribution of hydroxyl groups, it will form
comparatively long chains before branching occurs, so that the net effect
will be a bunching of crosslinks.

The second order rate constants which have been obtained
for the most important binder ingredients in order to establish their
relative reactivity are shown in Table 29. The kinetic runs were followed
by infrared. The concentration of the reactants (butyl isocyanate and the
binder components) was 1N in benzene. It is apparent from the rate data
that catalysis not only greatly accelerates the rate of reaction, but also
closes the gap between the less reactive and more reactive species. This
comparison does not include the effect of backbore structure which the
undiluted prepolymer mixture would exert on the rate and which is also over-
come by catalysis[10] (cf. Tables 1, 2 and 3). At this point it was of
interest to ascertain whether a low degree of catalysis in a binder system

TABLE 29

RELATIVE REACTIVITY OF SOME
BINDER COMPONENTS

IN In Benzene

Component	$Fe(AA)_3$ Concentration %	Temp. °C	$k_2 \; M^{-1} \; min^{-1}$
Polypropylene glycol (PPG)	--	25	0.9×10^{-4}
LHT-240[a]	--	25	1.0×10^{-4}
Glycerol triricinoleate (GTRO)	--	25	4.6×10^{-4}
242AM-310 (primary HTPB)	--	25	18.0×10^{-4}
LD-124[b]	--	25	16.0×10^{-4}
PPG	0.2	30	4.5×10^{-2}
LHT-240	0.2	30	5.5×10^{-2}
GTRO	0.2	30	8.1×10^{-2}
242AM-310	0.2	30	22.0×10^{-2}
LD-124	0.2	30	19.0×10^{-2}

[a] A low molecular weight polypropylene triol, often used as crosslinker in HTPB

[b] Polytetramethylene glycol (primary hydroxyls).

would yield different rubbers than the use of a higher level of catalyst.
The results of such a test are shown in Table 30 for HTPB Prepolymer Lot
242AM-310 (containing primary hydroxyl groups) crosslinked with GTRO or
LHT-240. The catalyst levels were 0.077% $Fe(AA)_3$ for the fast cure and
0.0007% $Fe(AA)_3$, inhibited by 0.014% HAA, for the slow cure. After the
specimens were well cured at 135°F (in two days) they were nevertheless
subjected for an additional 3 days to 180°F (in a N_2 atmosphere) to ensure
complete cure. Mechanical properties and swelling measurements were then
undertaken on the samples. Apparent crosslink density values are given,
calculated by the Flory-Rehner equation and a polymer-solvent interaction
parameter of 0.4 for the HTPB and 0.35 for the LD-124 rubber. The properties
of the LD-124 binder crosslinked with LHT-240 are included for comparison.
Here the effect of the slow cure is particularly pronounced, perhaps because
of the very low reactivity that LHT-240 would exhibit in an ether type
(hydrogen-bonding) solvent.

The data of Table 30 show a rather strong effect of slow
cure on properties. That the cure reaction was complete is beyond doubt,
since even the uncatalyzed binder would cure under these conditions. Whether
all of the effect is due to the different structure remains uncertain, since
side reactions can, of course, occur also. However, because a similar effect
can be produced much more elegantly by selectively prereacting the diol before
addition of the crosslinker, in which case the side reactions have the same
chances of occurring as in the binder made by simultaneous reaction of all
components, it is probable that the phenomenon is due to the same skewed
distribution of chain lengths.

4. Network Analysis

All these experiments indicate a strong dependence of
equilibrium swelling on chain length rather than on the number of effective
chains per unit volume of rubber network. Additional evidence for this
contention is the independence of the equilibrium swelling volume of rubbers

TABLE 30

EFFECT OF SLOW CATALYSIS ON BINDER NETWORK

Binder Composition, Parts	FeAA/HAA	σ_m, psi	ϵ_m, %	E_o, psi	$v_2^{(a)}$	$v_e \times 10^5$
242AM-310, 57.7; GTRO 7.1; HDI, 3.4; IDP 20	0.007/-	36	170	57	.124	5.6
Same	0.0007/ 0.014	25	123	51	.116	4.8
242AM-310, 57.7; LHT-240, 4.9; HDI, 3.4; IDP, 20	0.007/-	38	130	63	.138	7.7
Same	0.0007/ 0.014	30	120	51	.123	5.5
LD-124, 58.8; LHT-240, 4.8; HDI, 11.76; dibutyl phthalate 25	0.005/-	>282[b]	>650	162	.174	21.0
Same	0.0005/ 0.01	>128	>500	96	.085	3.8

[a] Swelling in benzene

[b] Dumbell specimen slipped unbroken from jig during test

on the extent of dilution prior to swelling. Inert diluents, like plasti-
cizers, incorporated into a rubber prior to cure, behave as if they were
the same volume fraction of parent rubber[13]. For example a given volume of
rubber cured in the presence of a plasticizer will expand on swelling to
the same size as an equal volume of an unplasticized rubber. In both of
these rubbers the effective chain length is the same, while the number of
chains is, of course, smaller in the plasticized elastomer. Semiconnected
chains affect swelling in the same manner as an equal volume of inert
diluent[14].

To summarize, it appears that the equilibrium swelling
volume of rubbers is essentially only a function of the chain length or
rather some chain length distribution, while mechanical properties depend
also on the number of chains, i.e., are affected by diluents, semiconnected
chains, etc.

In an attempt to explain these experimental results,
consider a three dimensional array of strands of rubber, which are tied
together randomly to simulate an actual rubber network. If these strands
are submerged in a swelling liquid, they will expand and the whole network
will expand isotropically as a consequence. With the expanding strands a
new volume is created which is not entirely filled by the swollen strand
but partly by pure solvent. Hence not all of the imbibed solvent is
actually used to solvate the rubber strands, a large portion of it just
fill the interchain created volume. In this volume, semiconnected chains
can be accommodated without requiring additional volume or solvent. Thus
a swollen rubber is visualized as a rather porous structure where a large
portion of the solvent is imbibed just to fill the interstitial space,
created by the expanding network, and is not really used to solvate the
network chains. If the network contained holes or other imperfections
prior to swelling, these will also expand isotropically during swelling.

For example filler particles, entrapped air bubbles, plasticizer, etc.
will not affect the final equilibrium swelling volume, and will behave as
if they were also rubber network.

So far this model explains the swelling behavior of network
containing fillers, plasticizers or other imperfections but does not cover
the effect of chain length distribution. From the observed effects we must
conclude that long chains contribute more to the volume increase than an
equal length of shorter chains. This effect of chain length is covered by
the following very simplified hypothesis.

Polymer chain statistics states that any two points on the
chain backbone separated by 50 or more chain atoms will be related to each
other in space according to a Gaussian distribution of vectors, and their
most probable distance will be proportional to the square root of the contour
length, ℓ, of the chain elements between these two points. On swelling, the
network expands and the distance, d, between these two points, which we may
consider to be branch points, increases. This increase in distance, Δd, we
assume to be proportional to the distance prior to swelling or

$$\Delta d = k\sqrt{\ell} \tag{16}$$

where k is a proportionality constant. In other words $\Delta d/\sqrt{\ell}$ is considered
constant for all chain lengths. The volume increase ΔV during swelling is

$$\Delta V = nc(d + kd)^3 - ncd^3 \tag{17}$$

where c is a proportionality constant depending on the geometry of swelling
and n is the number of chains per unit volume. Rearranging eq (17) yields,

$$\Delta V = ncd^3 \{(1 + k)^3 - 1\} = nc*d^3 = nc*\ell^{3/2} \tag{18}$$

where c* is a new constant.

The total swelling volume is

$$V_s = V_o + \Delta V, \qquad (19)$$

where V_o is the volume of the rubber prior to swelling. If we consider this rubber to be pure network rubber we may write

$$V_o = n^\ell g, \qquad (20)$$

where g is the cross section area of a chain. For simplicity, assume g to be unity. Introducing (18) and (20) into (19) yields

$$V_s = n\ell(1 + c*\sqrt{\ell}) \qquad (21)$$

The volume fraction of network rubber in the swollen gel, v_2, is

$$v_2 = V_o/V_s = 1/(1 + c** \sqrt{M}), \qquad (22)$$

considering that the contour length, ℓ, is proportional to the molecular weight, M, between branch points. Equation (22) was tested using a number of rubbers varying the crosslink density by changing the TP-2540/PPG ratio and using HDI as curative. TP-2540 and PPG contain the same backbone structure and the same type of OH groups so that the resulting network should contain the most random distribution of chain lengths possible to achieve. The exact composition of these binders is detailed in Table 31. From the composition M can be calculated if the exact functionality of the components is known. Although PPG type prepolymers are probably the best defined prepolymers on the market today, the actual functionality of TP-2540 may be between 2.9 and 3.0 and for PPG 1.95-2.0. Thus the error may be largest for the extreme cases in crosslink density. Furthermore, the cure reaction may not be 100% stoichiometric.

TABLE 31

COMPOSITION AND MECHANICAL PROPERTIES OF
PPG RUBBERS USED FOR TESTING THEORY

PPG[a]	TP2540	HDI	M_c[b]	Uniaxial Tensile Properties $\dot{\varepsilon} = 0.74$ Min^{-1}, 77°F			
				σ_m, psi	ε_m, %	E_o, psi	E^c
87.83	3.40	8.77	50,000	51	480	44	22
84.42	6.80	8.78	25,000	95	480	64	48
79.88	11.33	8.79	15,000	98	305	91	84
74.20	17.00	8.80	10,000	114	210	128	118
69.93	21.25	8.81	8,000	88	110	150	145
62.84	28.33	8.83	6,000	89	75	180	178
48.63	42.50	8.87	4,000	108	65	264	268
--	91.00	9.00	1,870	86	43	384	380

a Per 100 parts binder   0.1 part Fe(AA)$_3$ and 0.3 parts Neozone D were used.

b Calculated assuming strict trifunctionality of the TP2540 and difunctionality of PPG.

c Modulus determined by constant load creep test after 7 days.

Swelling data obtained in a number of solvents are shown as points in Figure 21, while Equation (22) is represented as solid lines. As evident from the figure the swelling data are reasonably well reproduced for the better swelling solvents chloroform, benzene, MEK and diethyl ether, moderately well for weaker solvents butyl ether and acetonitrile, and very poorly for the very weak solvents cyclohexane and hexane. Figure 22 shows the fit of the experimental data with the Flory-Rehner Equation (23) for a trifunctional network. The theoretical curves were derived using the average μ values calculated from the experimental points at 15000, 10000, 8000 and 6000 MW respectively, in the various solvents. The respective polymer-solvent interaction parameters were found to be: chloroform, 0.209; benzene, 0.335; MEK, 0.424; diethyl ether, 0.467; dibutyl ether, 0.524; acetonitrile, 0.614; cyclohexane, 0.660; hexane, 0.829. The best fitting data are found in the regime of μ factors between 0.3 and 0.5; acetonitrile is very poorly represented while the fit is better again for the very weak solvents cyclohexane and hexane.

Thus it appears that in the region of μ values between 0.2 and 0.5 both theories give about equivalent representation of experimental data. For rubbers that contain diluents or a larger fraction of ineffective structure, Equation 24 has to be used. At a μ factor of about 0.45 (natural rubber-benzene) the curves generated by each theory are so close that it is not possible to determine which gives the better fit experimentally (cf. Figure 23). In fact Lorenz and Parks[19] found that straight lines were obtained in plots of $1/Q^2$ vs $1/M_c$ for swelling measurements of sulfur and peroxide vulcanizates in benzene (Q is defined as grams solvent/grams rubber and is practically equivalent to $(1/v_2)-1$).

5. Effect of Bunching of Crosslinks on Mechanical Properties

Since slow cure can lead to bunching of crosslinks it was of interest to ascertain the effect on mechanical properties of the resulting

Figure 22

DEPENDENCE OF v_2 ON M FOR THREE μ VALUES

Solid lines Flory-Rehner:

$$-[\ln(1-v_2) + v_2 + \mu v_2^2] = 88.6M^{-1}(v_2^{1/3} - 2v_2/3)$$

$$(88.6 = \rho V_1)$$

Broken lines:

$$\left(\frac{1}{v_2} - 1\right)^2 = kM$$

$10^3 k = 2.05$

$10^3 k = 2.97$

$10^3 k = 3.97$

Figure 23
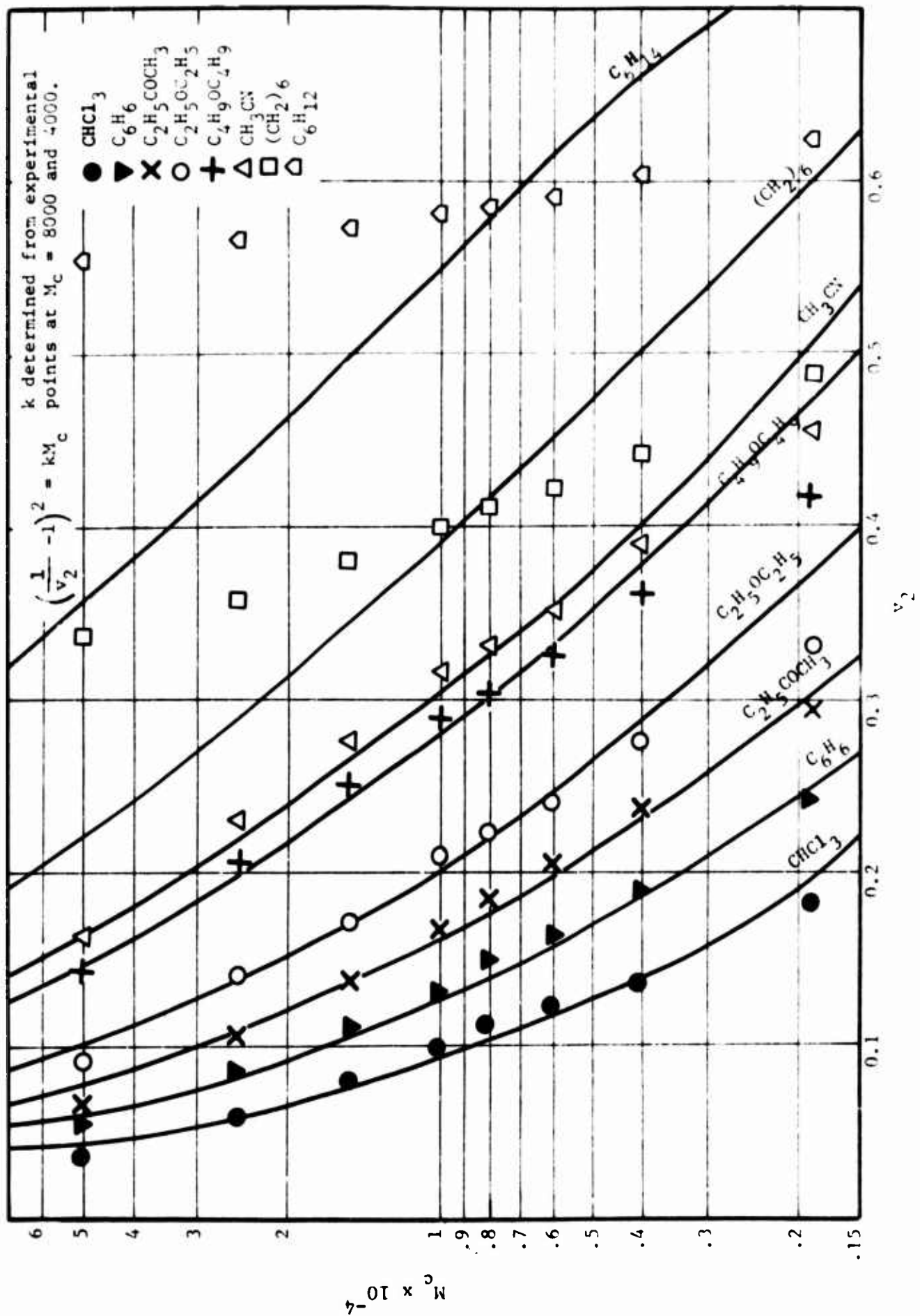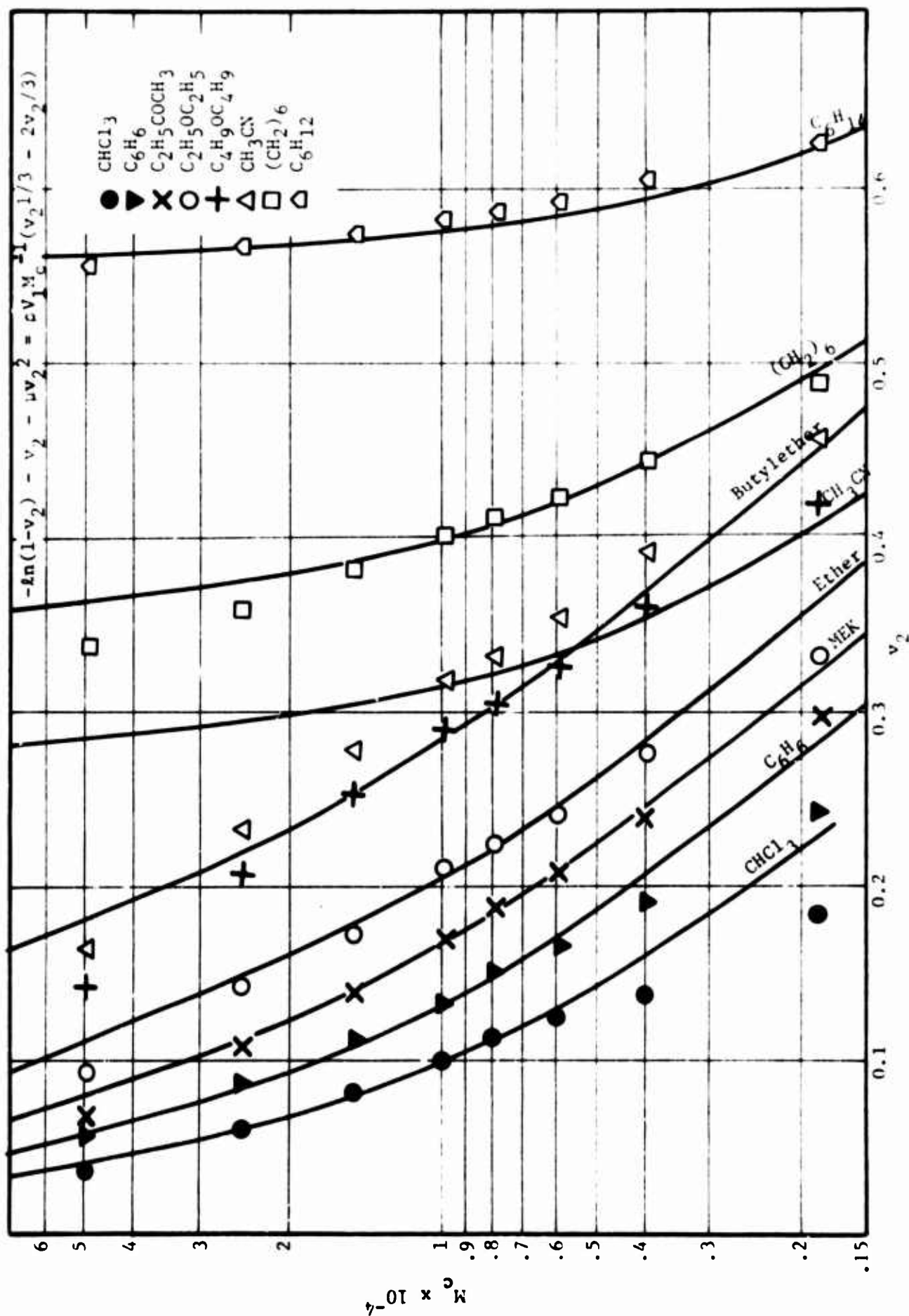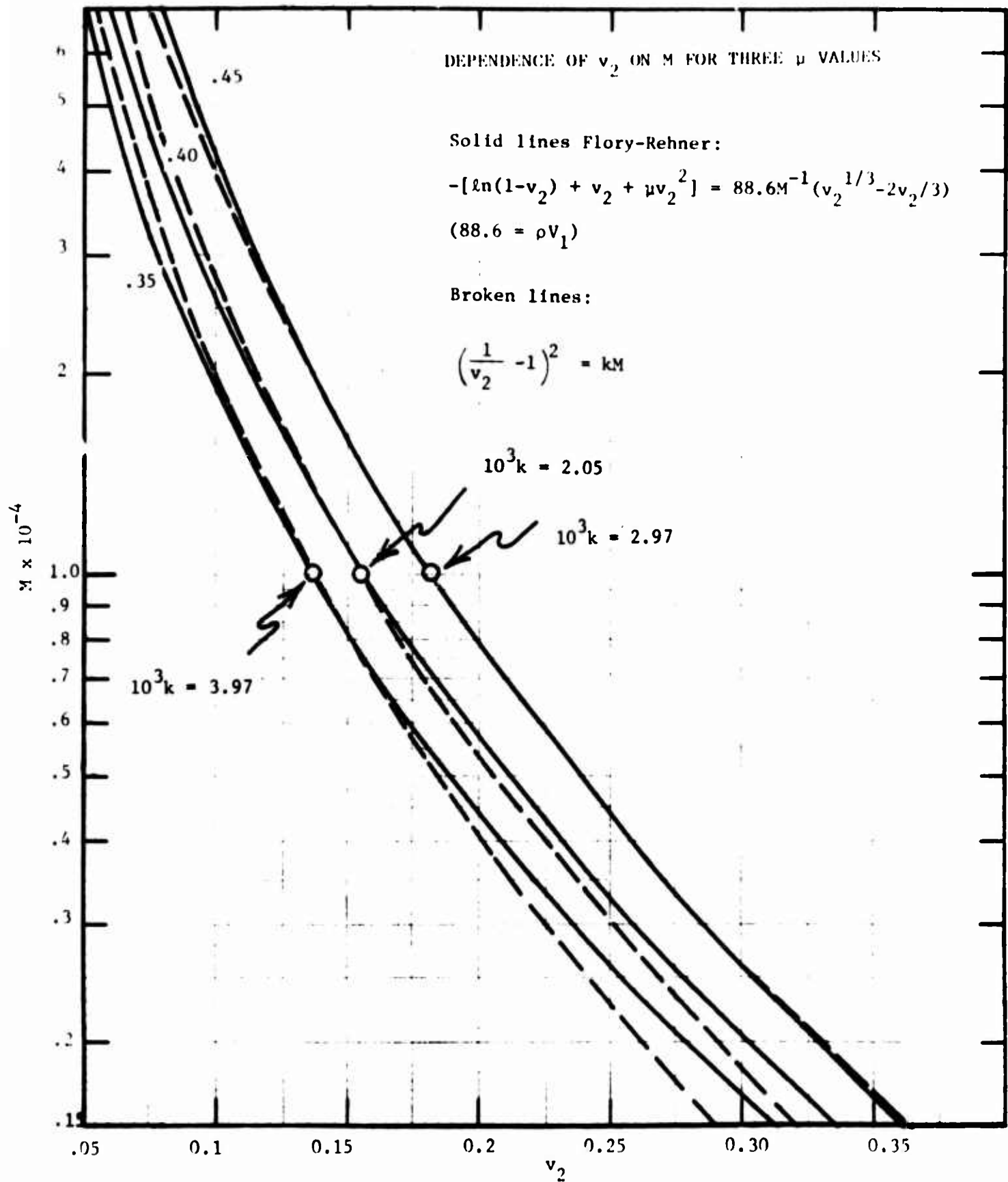
binders. To obtain this information the following experiments were conducted. A PPG-HDI prepolymer was prepared using 6 moles of PPG and 5 moles of HDI; the resulting diol should possess an average molecular weight of 11640 or an equivalent weight of 5820. This long chain PPG diol was then combined with various proportions of crosslinker (TP-2540) and cure was completed in the usual way under a N_2 atmosphere. All compositions contained in addition 0.3% Neozone D and 0.1% $Fe(AA)_3$. Table 32 shows the compositions in terms of equivalents of each component used. For comparison the equivalent binders, 1A to 6A, were prepared in which the prepolymer was replaced by the equivalent quantity of PPG and HDI. The data of Table 32 show that the rubbers containing the bunched crosslinks are always softer than their randomly crosslinked equivalent. In general, the mechanical properties are inferior. The higher stress decay of the bunched crosslink binders indicates the presence of longer chains than are present in the randomly crosslinked binders[14], which in Rubber 1, may be due to wider distribution of chain lengths. As stated previously, selective reaction can accentuate certain shortcomings in binder prepolymers the most serious of which is probably the formation of long monofunctional prepolymers if the functionality of the starting material is less than 2. This would lead to a high fraction of nonsupporting network structure in the final product, giving rise to inferior properties. However, such binders would not show the comparatively high stress decay which these binders exhibit, and therefore chain termination effects are not considered to play a large role. Nevertheless, whatever the case may be, selective cure reactions are in any case deleterious to good mechanical properties and should be avoided.

6. Determination of Crosslink Density of Propellant Matrix

Considerable work has been expended over the years to work out procedures which would yield the crosslink density of the propellant matrix. These procedures may be roughly divided into two classes: (1) dynamic measurements on swollen samples, usually compression modulus

TABLE 32

EFFECT OF BUNCHING OF CROSSLINKS ON EQUILIBRIUM SWELLING AND
MECHANICAL PROPERTIES OF PPG RUBBERS

Binder No.	Composition, Eq.			v_2^a	$v_e \times 10^4$	σ_m, psi	$\dot{\varepsilon} = 0.74$ min^{-1}, 77°F		
	Prepd.	TP2540	HDI				ε_m, %	E_o, psi	R^b
1	1	1	2	0.065	0.28	>50	>700	34	0.36
2	1	2	3	0.112	0.82	49	120	84	0.15
3	1	3	4	0.130	1.12	54	86	111	0.10
4	1	6	7	0.156	1.62	62	64	150	0.06
5	1	8	9	0.177	2.13	60	45	150	0.06
6	1	14	15	0.198	2.72	69	40	240	c
Equivalent Binders, Eq.									
	PPG	TP2540	HDI						
1A	6	1	7	0.093	0.57	>72	>470	67	0.20
2A	6	2	8	0.147	1.42	95	150	147	0.067
3A	6	3	9	0.159	1.69	87	100	165	0.03
4A	6	6	12	0.185	2.35	80	66	216	0.025
5A	6	8	14	0.199	2.75	84	50	240	0.02
6A	6	14	20	0.222	3.51	120	64	306	0.02

a Swelling in benzene, used μ of 0.30 for calculation of v_e according to Flory-Rehner.

b Relaxation test: Procedure - JANNAF bar was stretched one inch at a rate of 7.4 min^{-1}, then allowed to relax for two minutes. The stress decay is reported as the ratio.

$$R = \frac{\text{Stress immediately after stretching minus stress after 2 minutes}}{\text{Stress immediately after stretching}}$$

c Sample broke during relaxation.

determinations according to Cluff, Gladding and Pariser, and (2) determination of the volume fraction of rubber in the swollen matrix and use of the Flory-Rehner equation for a three functional network

$$M = \rho V_1 (v_2^{1/3} v_o^{2/3} - 2v_2/3)[\ln(1 - v_2) + v_2 + \mu v_2^2] \qquad (23)$$

In this equation ρ is the density of rubber matrix, V_1 is the molar volume of the swelling solvent and v_o is the volume fraction of rubber network in the matrix after cure, but prior to swelling.

Flory introduced the $v_o^{2/3}$ term to account for inert diluents which might be present in rubbers. It was, however, shown[13] that this correctional term is insufficient. It was found that in plasticized rubbers there exists a simple relation between v_2 of the unplasticized rubber and its prediluted counterpart. Prediluted means that the diluent was present during cure, i.e., during network formation. This relation is simply

$$v_{2,p} = v_{2,u} \cdot v_o \qquad (24)$$

where $v_{2,p}$ is the volume fraction of network rubber found in the equilibrium swollen, plasticized specimen, and $v_{2,u}$ is correspondingly the volume fraction of network rubber that would be found in the unplasticized specimen.

In these rubbers addition of plasticizers or diluents will not affect the length of the chains between branch points, since at least for polyurethane rubbers, the functional groups that react with each other are in fixed positions at the prepolymer chains. But also, in other vulcanizates, where crosslinking occurs randomly on the primary chain, the contour length of the chain between branch points will not be affected*. Since the crosslink density (number of chains/cm^3) but not the molecular weight between branch points is affected by diluents, Equation (23) is

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*This is readily realized if one considers that it does not really matter whether rubber molecules or solvent molecules solvate a given chain.

easily modified by introducing Equation 24, i.e.,

$$M = -\rho V_1 (v_p^{1/3} - 2v_p/3)/[\ln(1 - v_p) + v_p + \mu v_p^2] \qquad (25)$$

where $v_p = v_{2,p}/v_o$ which is identical numerically with $v_{2,u}$, but indicates a plasticized rubber. Equation (25) yields effective molecular weight between branch points irrespective of dilution. In order to derive the crosslink density, we have to consider the volume fraction of polymer network, viz

$$\frac{v_e}{V_o} = \frac{v_o}{M} \qquad (26)$$

In Figure 23 the dependence of M on v_2 is plotted for three solvent-polymer interaction parameters which most likely encompass the regime of HTPB-benzene swelling systems. For comparison, Equation (22) is also plotted. The values of the constants have been chosen such that the Flory-Rehner plot and Equation (22) are identical at $M = 10000$.

A simple example may illustrate some of the points made, and the use of Figure 23. Assume we swell a piece of urethane rubber of 1.0 density whose sol fraction is negligible, and find experimentally a v_2 value of 0.20. Assuming an interaction parameter of 0.40, from the Flory-Rehner plot, Figure 23, we find the M value to be 5600. If the same rubber composition were diluted 1:1 with an inert plasticizer ($v_o = 0.5$), we would find a v_2 value of 0.10. This would correspond to a molecular weight betwen branch points of 26000 which obviously is absurd. The corresponding crosslink density values are 1/5600 and 1/26,000, i.e., $= 1.78 \times 10^{-4}$ and 0.385×10^{-4} moles chains/cm^3 respectively. The crosslink density of the plasticized rubber should, however, be 1/2 that of the unplasticized rubber since we have the same number of chains in twice

the volume. The v_2 value that should have been used is $v_p = v_{2,p}/v_o = 0.20$ which inserted in Equation (23) or (25) yields the same molecular weight of chain segment between branch points as the undiluted rubber. Equation (26) yields the correct crosslink density for the rubber.

This incorrect accounting for the sol fraction is encountered very frequently. For example an equation used to derive v_2 from swollen propellant specimens is that of Bills,[20] slightly modified by Blatz and Lefferdink, viz:

$$1/v_2 = (1 + \frac{\Delta V_{ST}}{V_o} + v_{sol} v_f)/(1 - v_{sol}) \qquad (27)$$

where

ΔV_{ST}	is the swollen weight minus deswollen weight divided by density of solvent
V_o	is the volume of propellant before swelling
v_{sol}	is the volume fraction of sol in binder fraction
$1-v_{sol}$	is the volume of network over volume of binder or v_o
and v_f	is the filler fraction

Equation (27) is based on the concept that the solid filler behaves just like the same volume of matrix as far as this equilibrium swelling volume is concerned,[20] while plasticizers or other solubles in the propellant do not contribute to the swelling process and have therefore to be substracted.

The easiest way of determining the equilibrium swelling volume and thus v_2 of the propellant matrix, of composite propellants, is by measuring the lengths of the unswollen and swollen specimen.

Then

$$v_2 = (\ell_o/\ell_s)^3 \tag{28}$$

where ℓ_s is the swollen and ℓ_o the unswollen lengths of the propellant specimen. It is, of course, important, that the matrix releases from the filler during the swelling process.

Dynamic measurements on swollen propellants have been repeatedly carried out by a number of workers, and the data were used to calculate the crosslink density according to the well known formulas of the theory of elasticity or Mooney-Rivlin. These measurements usually consist of determinations of compression modulus or tensile modulus in the swollen state. However, this author knows of no work which has considered the effect of the solvent pockets formed during swelling of composites around the solid filler, on the modulus. A swollen composite may be considered as a liquid filled foam. Foams differ in their mechanical properties significantly from the parent rubber. For example the modulus of a foam, containing 50% rubber, is only 1/4 that of the nonporous parent rubber, and similar relations hold for liquid filled foams[13]. Consequently these measurements are apt to indicate a considerably lower crosslink density of the matrix rubber than is actually the case. Presently there is no adequate theory to account for this effect.

Actual propellant swelling data will be presented later in this report.

D. DEVELOPMENT OF CATALYSTS FOR AMBIENT TEMPERATURE CURE

    1. Urethane Catalysts in the Presence of Moisture

In the first sections of this report, the activity of various catalysts towards aqueous and alcoholic hydroxyl groups was compared. For example, it was found that the $Fe(AA)_3$ catalyzed urethane reaction is about

500 times faster than the catalyzed urea reaction and that for T-12, this
ratio is less favorable (30 times). Catalyst degradation by hydrolysis
in case of $Fe(AA)_3$ can be ruled out as an explanation for the relatively
much higher activity of the $Fe(AA)_3$ as urethane catalyst. Although hy-
drolysis was found to inactivate lead, divalent tin and zinc catalysts,
$Fe(AA)_3$ was not degraded in these tests. Addition of fresh HDI to the spent
reactant mixture immediately caused further reaction. These results indicate
that moisture interference in $Fe(AA)_3$ catalyzed urethane reactions may not
play much of a role in cure failure, if urea and urethane reaction proceed
essentially independent of each other.

This premise, which is a common kinetic consideration, was
put to test in the following experiment. To a PPG type polyether binder,*
shown below, an approximately equivalent quantity of water was added. Cure
was attempted, using various catalysts.

	Grams	Equivalents
TP-2540	12	0.014
PPG	79	0.087
HDI	9	0.107
H_2O	1	0.111
Neozone D	0.1	-
Catalyst	0.05	-

If the urethane reaction is significantly faster than the
water-isocyanate reaction, cure should be obtained. However, specimens
cured only when the isocyanate concentration approached stoichiometry
including the reaction of the water (in the above case around 0.2 - 0.22
equivalents).

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*Only polyoxypropylene diols and triols are capable of dissolving the
 required quantity of water (PPG dissolves approximately 2% water at room
 temperature).

There were slight differences among the various metal catalysts. Fe(AA)$_3$ seemed to require a little less HDI than T-12. Lead naphthenate and octoate did not cure at all. Infrared analysis in the latter cure specimens showed high NCO absorption indicating that the catalyst had degraded and became ineffective in promoting cure. These results show significant interference by moisture and appear at first irreconcilable with the rate data shown in Table 16. Therefore, additional rate studies were made of solutions which contained both alcohol and water. Data shown in Table 33 indicate quite clearly that there must be strong interference of the urethane reaction by moisture, since the rate of conversion decreases with addition of water. If the reactions proceed independently, conversion should be greater in the case of the butanol-water reaction. Figures 24 and 25 show the conversion versus time plots of these reactions.

The rate constants tell nothing about the products formed during this reaction. Therefore, to determine the relative rate with which each of these reactions proceeds, the following test was designed. To an acetone solution of methanol and water (each one molar) was added 1 mole of either butyl isocyanate or phenyl isocyanate. The solutions were catalyzed at the 0.2% level with various catalysts. After 3 days at room temperature, the resulting mixtures were analyzed for dibutylurea and diphenylurea respectively. In the case of the dibutylurea, separation from the methyl butylcarbamate proved to be practically impossible, since both products appear to have nearly the same solubility in the various solvents. After some experimentation it was found best to use the refractive index at 50°C of the mixture, from which solvent and excess H_2O and CH_3OH had been removed, as a measure for the concentration of the dibutylurea formed. Its concentration was established by comparison with a calibration curve constructed from various proportions of the pure compounds. Note: dibutylurea melts at 73°C, methyl butylcarbamate is a colorless liquid b.p. 192°C. At room temperature a 40% solution of dibutylurea in the urethane is still

TABLE 33

CATALYZED REACTION BETWEEN BuOH AND HDI AND BuOH, H_2O, HDI IN ACETONE

at 30°C

Reaction and Molarity	Catalyst [a]	$k_2[M^{-1} min^{-1}]$
BuOH 1.07, HDI 0.25	$Fe(AA)_3$	0.23
BuOH 1.07, HDI 0.25	T-12	0.093
BuOH 1.07, H_2O 1.1, HDI 0.25	$Fe(AA)_3$	0.084
BuOH 1.07, H_2O 1.1, HDI 0.25	T-12	0.041

[a] 0.2%

TIME VS CONVERSION PLOTS OF EtOH-HDI AND BuOH-H₂O-HDI
REACTIONS CATALYZED WITH T-12
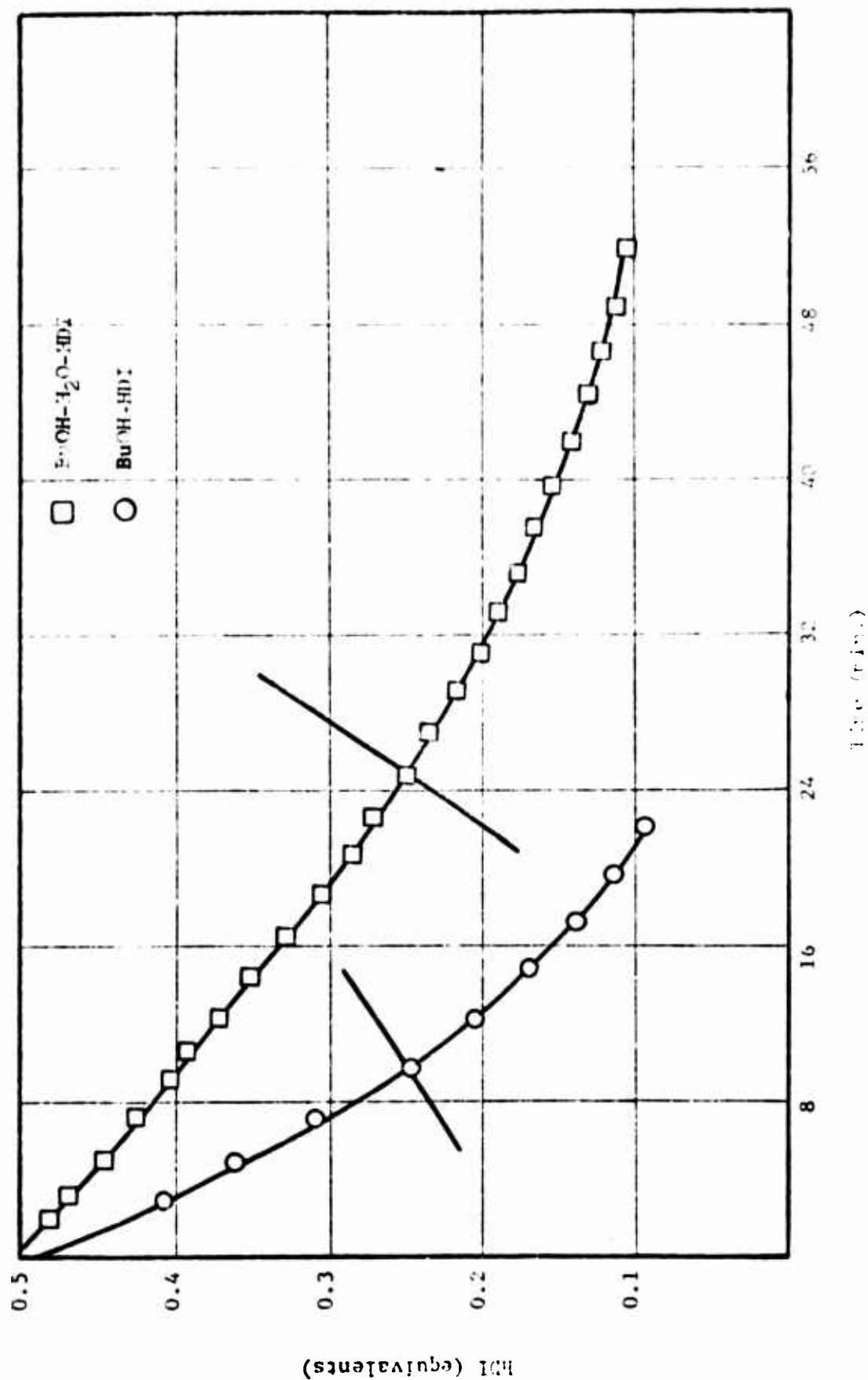
Time (min.)

HDI (equivalents)

Figure 24

TIME VS CONVERSION PLOTS OF BuOH-HDI AND BuOH-H$_2$O-HDI
REACTIONS CATALYZED WITH Fe(AA)$_3$

Figure 25
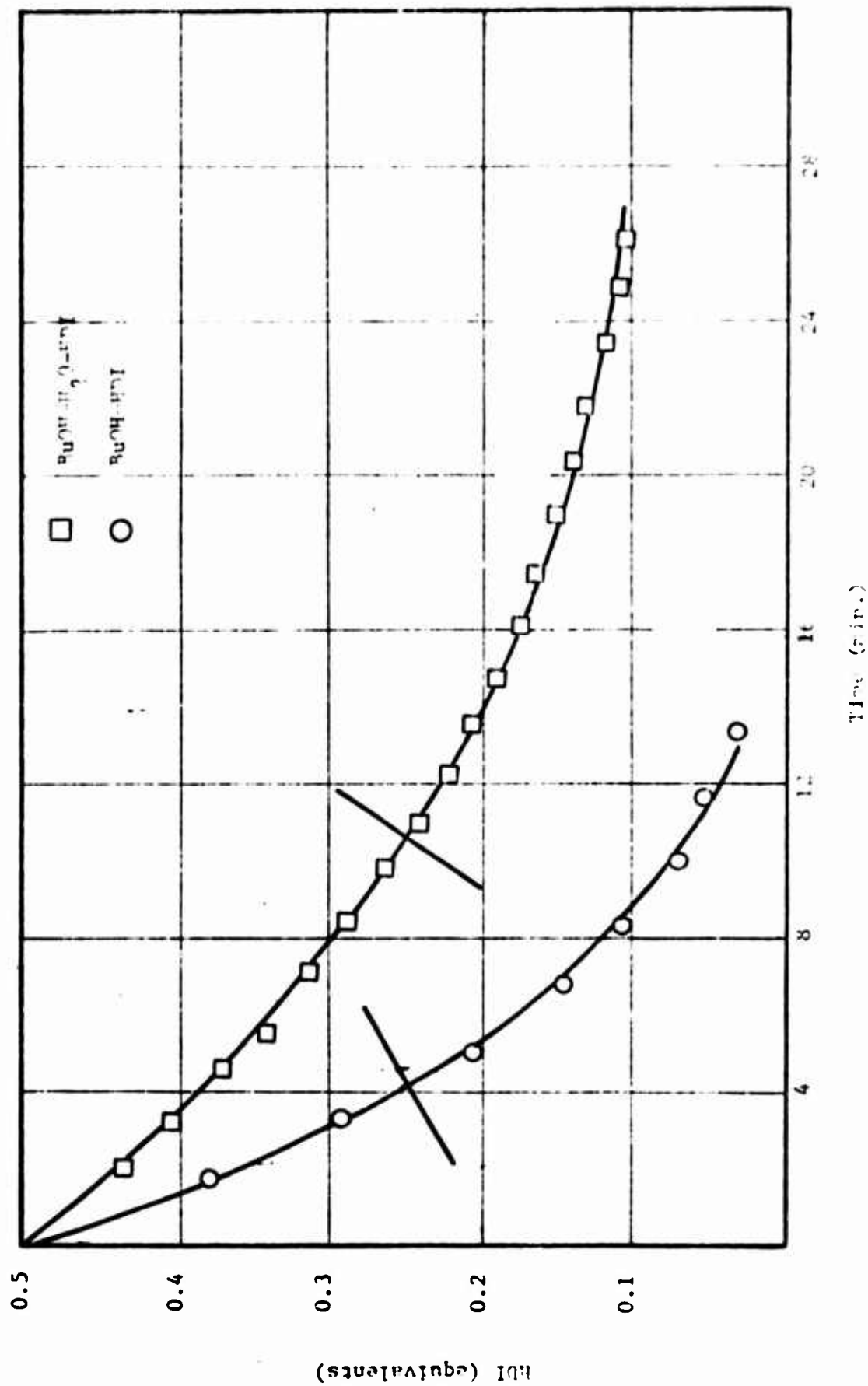
liquid. In case of the phenyl isocyanate, the reactant mixture was concentrated by removing excess solvent, H_2O and CH_3OH. Then the mixture was digested with benzene which dissolves the methyl carbanilate but not the diphenylurea. The latter was filtered and weighed. Table 34 lists the results of these tests. The urea concentration is given in terms of percent of isocyanate converted to urea. The difference from 100 is essentially the quantity of urethane formed, since homopolymerization under these conditions is insignificant. It may be mentioned here that similar tests were run using HDI and TDI, but because of the much greater variety of species formed, analysis of the products become very complicated. Some of these species are $H_3COCOHN(CH_2)_6NHCOOCH_3$, simple urethane: $H_3COOCNH(CH_2)_6NHCONH(CH_2)_6NHCOOCH_3$, simplest urea - urethane; $H_3COCOHN(CH_2)_6NHCONH(CH_2)_6NHCONH(CH_2)_6NHCOOCH_3$, di urea - urethane; etc. Several of the results shown in Table 34 are noteworthy: (a) both aliphatic and aromatic isocyanates (probably this generalization is permissible) yield similar ratios of urethane/urea with the various catalysts, and (b) in the uncatalyzed mixtures this ratio is smallest, i.e., the desired urethane reaction is the most inhibited. In other words catalysis brings about a definite shift favoring urethane formation. In some tests (lead naphthenate, $Pb(AA)_2$, tin octoate, tin naphthenate, $Zn(AA)_2$ and $TiO(AA)_2$) the catalyst becomes so inactivated through hydrolysis that reaction is not complete after 4 days. Obviously in such cases the composition of the product is affected, since the uncatalyzed reaction will proceed to a considerable extent.

The high concentration of urea formed in the presence of an alcohol when catalysts are used indicates that the reactions do not proceed independently of each other. Otherwise the yield of urea and urethane should be proportional to the velocities of the pure reactions. Although the mechanism of the catalyzed water-isocyanate reaction is not known, it is believed to be similar to the one proposed for the metal catalyzed urethane reaction, viz.

TABLE 34

UREA FORMED IN THE CATALYZED REACTION OF MeOH, H_2O, BuNCO IN ACETONE,
AND MeOH, H_2O, ØNCO IN ACETONE ALL 0.96M

At Ambient Temperature

Catalyst[a]	Percent of the Isocyanate Converted to Urea	
	BuNCO	ØNCO
None[b]	>75	55
Fe(AA)$_3$	9	10
Mn(AA)$_3$[c]	5.5	5
In(AA)$_3$[c]	43	47
Th(AA)$_4$[c]	57	49
Zr(AA)$_4$[c]	52	59
Zn(AA)$_2$[b,c]	56	51
UO$_2$(AA)$_2$	10	19
V(AA)$_3$	26	26
Zn Decanoate[c]	36	47
Pb(AA)$_2$[b,c]	(37)	not tested
MoO$_2$(AA)$_2$	26	30
Pb Naphthenate[b,c]	(59)	not tested
Sn Octoate[b,c]	(46)	42
Sn Naphthenate[b,c]	(44)	39
Dibutyltin Dilaurate	14	18
Dibutyltin Diacetate	17	18
Cu(AA)$_2$	30	44
TiO(AA)$_2$[b,c]	>75	46

[a] 0.2%

[b] BuNCO solutions had not completely reacted during 4 days. Catalyst was inactivated by moisture and the composition of the mixture at this stage is essentially uncatalyzed. The same holds for ØNCO, but the higher reactivity of the isocyanate results in complete reaction whether catalyzed or not.

[c] Catalysts gave indication of hydrolysis by formation of a cloudy precipitate.

$$Fe(AA)_3 + 2ROH \; \rightleftharpoons \; [Fe(AA)_2(OR)_2]H + HAA \qquad\qquad I$$

$$[Fe(AA)_2(OR)_2]H + R'NCO \; \rightleftharpoons \; [Fe(AA)_2(OR)_2]..OCNHR' \qquad II$$

$$[Fe(AA)_2(OR)_2]..OCNHR' \; \rightarrow \; R'NHCOOR + Fe(AA)_2OR \qquad III$$

$$Fe(AA)_2OR + ROH \; \rightleftharpoons \; [Fe(AA)_2(OR)_2]H \qquad\qquad\qquad IV$$
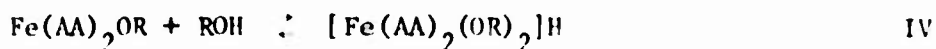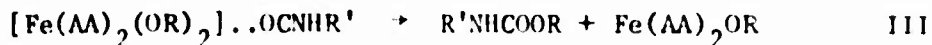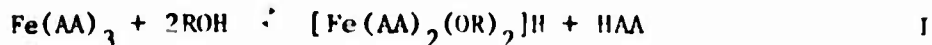
In Step I alcohol enters the catalyst molecule freeing HAA and forming an acidic species (alkoxo acid). This reaction accounts for the inhibition of catalysis by acetylacetone. In Step II the activated complex is formed, whose rearrangement to the product urethane (Step III) is the slow, rate determining reaction in the sequence. In IV the catalytic species is regenerated by adding another molecule of alcohol to reform the alkoxo acid. Reactions I and II are very fast and equilibrium is achieved practically immediately upon mixing of the reactants as ascertained from spectroscopic evidence. Hence Step III, the rearrangement, must be the critical factor governing the velocity of the reaction. Thus the rate of the catalyzed reaction depends on two parameters: the concentration of the activated complex, given by the two preceeding equilibria, and its stability. The less stable this complex, the faster is the rearrangement and thus the velocity of the catalyzed reaction. The stability of the complex is probably a function of the acid strength of the alkoxo acid. A very strong acid gives intermediates which are indefinitely stable, e.g., RNCO + HCl = RNHCOCl, although they will react with alcohol to form urethane with liberation of the acid. Because of the higher acidity of H_2O the resulting alkoxo acid is stronger than that of the alcohols which will in turn yield a more stable intermediate. Another possibility is the formation of mixed water-alcohol complexes. Probable configurations are

$[Fe(AA)_2(H_2O)OH]H$ $[Fe(AA)_2(H_2O)(OR)]H$

I $[Fe(AA)_2(OH)(ROH)]H$

Hydroxo-acid   II

Mixed hydroxo-alkoxo acid
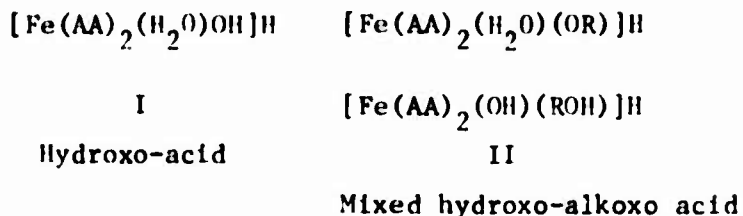
The rearrangement of the activated complex formed between I and RNCO is slow as we know from the catalyzed water-isocyanate reaction in the absence of alcohol. The activated complex formed between II and an isocyanate, however, could account for the observed proportions of products and rates. Figures 24 and 25 and Table 33 show that the catalyzed rates of the H_2O-BuOH-HDI reaction are indeed slower than those of the BuOH-HDI reaction, which agrees with the proposed higher stability of the activated complex. It also should be borne in mind that all of the active species, namely, compounds I, II and the alkoxo acid depicted in Step II of the reaction sequence are products of simultaneous equilibria and their concentration is governed by the quantity of liberated HAA. Thus the relative quantity of active species will depend on the equilibrium constant for that reaction. It stands to reason that the equilibrium constant for the $Fe(AA)_3$-H_2O dissociation reaction is much larger than that for the $Fe(AA)_3$-ROH alcoholysis, owing to the much greater acidity of H_2O and stability of the resulting product, e.g., $Fe(AA)_2OH$ is known and has been isolated (21), which was not possible for the alkoxo acid (11). Therefore, the concentration of $[Fe(AA)_2(OR)_2]H$ is probably very small compared to that of the active species I or II, respectively.

2. Catalyst Modification

$Mn(AA)_3$ and $Fe(AA)_3$ emerged as the two most discriminating urethane catalysts, i.e., they yield the highest concentration of urethane in the presence of water. Both are rather efficient catalysts and in this

respect, pose problems of short potlife with HTPB prepolymers. In addition,
$Mn(AA)_3$ shows rather poor hydrolytic stability decomposing readily in the
presence of moisture. Therefore, a number of Mn^{3+} and Fe^{3+} chelates were
prepared and tested for hydrolytic stability, catalytic efficiency and
ability to discriminate between aqueous and alcoholic hydroxyl groups.
Their effect on HDI homopolymerization has also been ascertained.

The guiding thoughts for the preparation of these compounds
were: (1) sufficient chelate stability to improve resistance to hydrolysis,
particularly with manganic compounds, (2) reduction of catalytic efficiency
to improve potlife and (3) investigation of different ligands with respect
to their effect on the catalyst's ability to differentiate between water and
alcohol. The preparation of the compounds is briefly outlined below.

a.   Ferric Acetoacetate
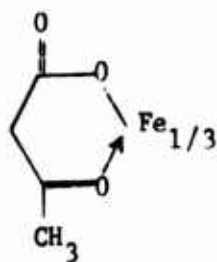
It was thought that β-keto acids might produce chelates
which are particularly stable against hydrolysis since the enolic hydroxyl
group of the acetylacetone is replaced by the more acidic carboxyl group.
However, this premise proved wrong. Ferric acetoacetate was obtained only
in aqueous solution, which slowly decomposes on standing. Preparation: To
0.1 moles of ethyl acetoacetate is added 100 cc of 1N aqueous potassium hydroxide.
The resulting clear, yellowish solution was allowed to stand in the refriger-
ator for two weeks. To the solution of potassium acetoacetate are added 100 ml
of 1N $FeCl_3$ in water, whereupon the solution immediately assumes a deep

brown-red color. Every attempt to isolate the compound proved futile. On evaporation to dryness in vacuo, decomposition to $Fe(OH)_3$ occurred.

b. Ferric o-Formylphenolate
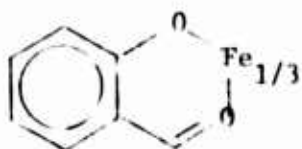
To a solution of 9g $FeCl_3 \cdot 6H_2O$ in water are added 12.2g salicylic aldehyde. To this mixture are added 100 ml of 1N KOH in MeOH while stirring. Blood-red precipitate occurs, strongly resembling $Fe(AA)_3$. This is filtered and dried in air, finally in vacuum. Note: This compound hydrolyzes very readily if in solutions of alcohol, acetone and benzene. The reason it can be made from aqueous solution is probably its very low solubility in H_2O.

c. Ferric Trifluoroacetylacetonate, $Fe(F_3AA)_3$
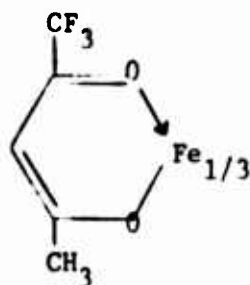
An equinormal alcoholic solution of $FeCl_3$ and tri-fluoroacetylacetonate is neutralized with alcoholic KOH. The KCl is filtered, and the remaining solution is concentrated until crystallization begins. $Fe(F_3AA)_3$ is filtered and may be recrystallized from benzene-hexane.

d. Ferric Hexafluoroacetylacetonate, $Fe(F_6AA)_3$

Same procedure as for $Fe(F_3AA)_3$

e. Ferric 1-Phenyl-1,3-butanedionate, $Fe(PhAA)_3$

Same procedure as for $Fe(F_3AA)_3$
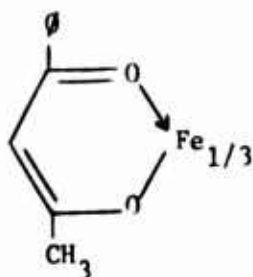
f. Ferric 1,3-Diphenyl-1,3-Propanedionate, $Fe(Ph_2AA)_3$

Same procedure as for $Fe(F_3AA)_3$
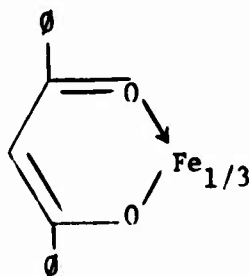
g. Ferric Dehydracetate, $Fe(DAc)_3$

Same procedure as for $Fe(F_3AA)_3$
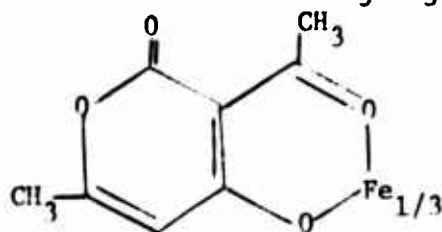
h.   Ferric 1,1-diacetylacetonate, Fe(TAM)$_3$

Same procedure as for Fe(F$_3$AA)$_3$
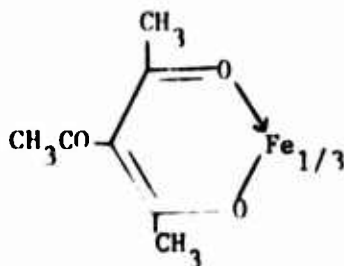
The triacetylmethane was prepared from potassium acetylacetonate and acetyl chloride. B.P. 111°/22 mm/Hg.

i.   Ferric 8-Hydroxyquinolate, Fe(HQ)$_3$

Same procedure as for Fe(F$_3$AA)$_3$.

j.   Manganic 1,3-diphenylpropane-1,3-dionate, Mn(Ph$_2$AA)$_3$ can be prepared according to the procedure for Mn(AA)$_3$: Inorg. Synthesis, 5, 188 (1957). A convenient shortcut is as follows: To a concentrated solution of Mn(AA)$_3$ in MeOH is added a slight stoichiometric excess of di-benzoylmethane. After a short while Mn($\emptyset_2$AA)$_3$ starts to precipitate. It is filtered and recrystallized from benzene-hexane. In like fashion (k) and (l) are prepared conveniently from commercial Mn(AA)$_3$ and dehydracetic acid or 8-hydroxyquinoline, respectively.

k.   Manganic dehydracetate, Mn(DAc)$_3$

See (j) above.

l.   Manganic 8-hydroxyquinolate, Mn(HQ)$_3$

See (j) above.

3. Efficiency of Catalysts

The activity of most of these compounds is shown in Table 35. As a rough rule it appears that the catalytic activity of the chelates decreases as the chelate stability increases. This fact, however, is sometimes obscured by the insolubility of the catalyst. Stability tests of most compounds are reported in Section D5. The chelate stability appears to increase with increasing acidity of the diketone, i.e., its degree of enolization. The acidity, in turn, increases with electronegative substitution of the parent acetylacetone. Steric effects and solubility also play a large role. For example, $Fe(DAc)_3$ and $Mn(DAc)_3$ are very difficultly soluble in most solvents.

Ferric 8-hydroxyquinolate is the most stable iron complex shown in Table 35. Its low catalytic activity is further accentuated by its very low solubility.

The ability of the catalysts to discriminate between aqueous and alcoholic hydroxyl groups is shown in Table 36. Two runs were made in order to gain information on the precision and/or reproducibility of this test. Table 36 lists the results reported previously as well as the repeat runs. The repeat runs differ from the first test series by longer duration (7 days). Table 36 indicates good reproducibility for this rather complex reaction. Thus it appears that open chain compounds like $FeCl_3$, ferric octoate, and (probably) ferric glycinate are definitely inferior in their ability to differentiate between water or alcohol. The high proportion of urea in the ferric salicylaldehyde complex is probably a consequence of the fast decomposition of that compound and the ensuing uncatalyzed reaction, which produces essentially urea. In case of the $Cr(HQ)_3$ the high urea content is probably again due to the uncatalyzed reaction because of the very low catalytic activity of the chromium compound. Low catalytic efficiency or catalyst decomposition can be detected by the low yield of product.

TABLE 35

ACTIVITY OF IRON AND MANGANIC CHELATES BuOH (0.88M) - HDI (0.52M) REACTION IN ACETONE AT ROOM TEMPERATURE

Reaction Followed by Infrared

Compound	$10^2 k_2 E^{-1} min^{-1}$
$FeCl_3$	1.7[a]
$Fe(AA)_3$	19.0
$Fe(F_3AA)_3$	11.3
$Fe(F_6AA)_3$	0.97[a]
$Fe(PhAA)_3$	7.0
$Fe(Ph_2AA)_3$	6.7
$Fe(TAM)_3$	14.2
$Fe(Octoate)_3$	0.61
$Fe(Glycinate)_3$	0.47
$Fe(o-Formylphenolate)_3$	30.71
$Fe(HQ)_3$	1.5[b]
$Fe(DAc)_3$	8.5
$Mn(AA)_3$	27.0
$Mn(Ph_2AA)_3$	8.3
$Mn(DAc)_3$	1.9
$Mn(HQ)_3$	4.9
$Cr(HQ)_3$	0.018
Control	<0.001

[a] Catalyst appears to decompose during reaction. $FeCl_3$ has a very fast start, then rate tapers off rapidly.

[b] Catalyst not completely soluble.

TABLE 36

PERCENT OF DIBUTYLUREA IN THE REACTION PRODUCT OF MeOH AND
H_2O WITH BuNCO: REACTION TIME 4 DAYS AT ROOM TEMPERATURE

CATALYST CONCENTRATION 0.10%

$[H_2O]$ = [MeOH] = 1M; [HDI] = 0.5M

	% Urea, after	
	4 days	7 days
$FeCl_3$	44	–
$Fe(AA)_3$	7	6
$Fe(F_3AA)_3$	7	4
$Fe(F_6AA)_3$	44	39
$Fe(PhAA)_3$	12	6
$Fe(Ph_2AA)_3$	8	6
$Fe(Octoate)_3$	26	23, 30
$Fe(Glycinate)_3$	29	nt
$Fe(o-Formylphenolate)_3$	39	nt
$Fe(HQ)_3$	nt	3, 4
$Fe(DAc)_3$	6	5
$Mn(AA)_3$	6	5
$Mn(Ph_2AA)_3$	6	8
$Mn(HQ)_3$	6	6
$Mn(DAc)_3$	nt	13
$Cr(HQ)_3$	nt	33
Control	nt	>50

nt = no test was made

For example, after 7 days reaction time, the yield of product (urea + urethane combined) for the $Fe(AA)_3$ catalyzed sample was 5.48g (about theoretical for urethane in this test) while it was 0.90g for the un-catalyzed reaction, 1.68g for $Cr(HQ)_3$, and 1.91g for the ferric salicylaldehyde complex catalyzed reactions, respectively.

4. Homopolymerization

Table 37 shows the result of homopolymerization studies conducted with these catalysts. A few copper chelates in which the chelate ring was modified are included. Bivalent Ni and Co compounds have also been added in order to ascertain whether the planar structure of the coordinatively four valent metal ion could be responsible for the strong homopolymerization efficiency of the $Cu(AA)_2$. Since $Ni(AA)_2$ or $Co(AA)_2$ do not greatly accelerate HDI homopolymerization this structural characteristic is probably insignificant. However, it is very interesting to note that the modified $Cu(AA)_2$, namely the Cu-1 and Cu-2 compounds, show little homopolymerization tendencies. The same holds for the copper chelate formed with the addition product of one mole isopropylenediamine and salicylaldehyde. However, these copper compounds did not yield satisfactory cures. All of the tested iron and manganese compounds, perhaps with the exception of ferric oleate, accelerate homopolymerization to about the same extent. The slight differences may be due to differences in solubility, and are deemed insignificant.

5. Stability Towards Hydrolysis

$Fe(AA)_3$ and particularly $Mn(AA)_3$ are susceptible to hydrolysis and may therefore become inactivated during cure. The test adopted to get a more quantitative measure consists of determining the absorbance at a characteristic wave length of a catalyst dissolved in MEK containing 2% water. In these tests, the catalyst concentration was 0.04% and the absorbance was measured in pure MEK and after 1 day standing in MEK containing

TABLE 37

% HDI REMAINING UNCHANGED AFTER 5 DAYS STORAGE AT ROOM TEMPERATURE OF A 10% SOLUTION IN TOLUENE.

Catalyst concentration 0.04%

Catalyst	% NCO left
None	100
$FeCl_3$	93
$Fe(AA)_3$	94
$Fe(F_3AA)_3$	89
$Fe(F_6AA)_3$	89
$Fe(PhAA)_3$	92
$Fe(Ph_2AA)_3$	89
$Fe(HQ)_3$	94
$Fe(DAc)_3$	94
$Fe(o-formylphenolate)_3$	90
$Fe(Oleate)_3$	84
$Fe(Glycinate)_3$	98
$Mn(AA)_3$	91
$Mn(Ph_2AA)_3$	93
$Mn(HQ)_3$	92
$Cu(AA)_2$	22
$Cu(HQ)_2$	96
Cu-1[a]	89
Cu-2[a]	94
Cu-3[b]	89
Co-1	92
$Ni(AA)_2$	87
$Co(AA)_2$	92

---

[a] Modified $Cu(AA)_2$

[b] Chelate with addition product of $H_2NCH_2CHNH_2CH_3$ and $o-C_6H_4(OH)CHO$

2% H_2O. The absorbance value in pure MEK was taken to be 100. From the ratio of the absorbances of nonaged and aged solutions the percent catalyst decomposed during aging have been calculated and are given in Table 38. The absorbances were obtained in a 0.2 cm cell in a Ratio Recording Beckman Spectrophotometer. The solutions not completely decomposed during 1 day at room temperature were placed into a 50°C oven for an additional day.

Increasing the acidity of the ligand definitely improves the hydrolytic stability. Thus Ph_2AAH is more acidic than PhAAH, which is more acidic than HAA, and the stability of the corresponding ferric dionates has a similar order. Although $Mn(Ph_2AA)_3$ also was completely hydrolyzed under the conditions of this test, it was definitely more stable than $Mn(AA)_3$. The latter immediately forms a floculent precipitate upon the addition of water, while it takes a few hours for $Mn(Ph_2AA)_3$ to decompose.

6. Cure Tests of Modified Catalysts

a. Binders

The above catalysts were also tested for efficiency in a polypropylene oxide binder of the following composition: TP-2540, 12 parts; PPG, 79 parts; HDI, 9 parts; Neozone D, 0.2 parts; catalyst, 0.1 percent. Cure results are listed in Table 39.

In HTPB binders such cure tests are of little heuristic value, since even the uncatalyzed binder will eventually cure.

Under the conditions of this test all catalysts with the exception of the very insoluble $Fe(HQ)_3$ and some Cu compounds produced cure. Even the rather instable manganic chelates gave cured binders. However, it must be pointed out, that in this test the cure reaction is pushed so fast, that catalyst instability plays a minor role only. In propellants,

-141-

TABLE 38

DECOMPOSITION OF CATALYSTS (0.04%) IN MEK
CONTAINING 2% H_2O

	Per Cent of Catalyst Decomposed	
	After 1 Day at Room Temp.	Additional Day at 50°C
Fe(AA)$_3$	41	95
Fe(F$_3$AA)$_3$	16	54
Fe(F$_6$AA)$_3$ [a]	76	100
Fe(PhAA)$_3$	30	84
Fe(Ph$_2$AA)$_3$	20	76
Fe(DAc)$_3$	52	94
Fe(HQ)$_3$	0	0
Fe(o-Formylphenolate)$_3$	86	100
Fe(Octoate)$_3$	-	90
Mn(AA)$_3$	100	-
Mn(Ph$_2$AA)$_3$	100	-
Mn(HQ)$_3$	0	28

(a) Fe(F$_6$AA)$_3$ appears to be unstable even in the absence of H_2O, evidenced by a yellowing of the initially red solution.

TABLE 39

CURE EFFICIENCY OF VARIOUS CATALYSTS (0.1%) IN POLYETHER BINDER

	Binder Cure at Room Temp. After		
	3 Hrs	16 Hrs	3 Days
$Fe(AA)_3$	c	c	c
$Fe(F_3AA)_3^{(pi)}$	nc	sc	sc
$Fe(F_6AA)_3^{(pi)}$	nc	sc	sc
$Fe(PhAA)_3^{(pi)}$	nc	sc	c
$Fe(Ph_2AA)_3^{(i)}$	sc	c	c
$Fe(HQ)_3^{(pi)}$	nc	nc	nc
$Fe(Octoate)_3$	sc	sc	c
$Fe(Glycinate)_3^{(pi)}$	nc	nc	sc
$Fe(o-Formylphenolate)_3^{(pi)}$	nc	nc	sc
$Fe(DAc)_3^{(pi)}$	nc	nc	sc
$Mn(AA)_3$	c	c	c
$Mn(Ph_2AA)_3^{(pi)}$	nc	nc	sc
$Mn(HQ)_3$	nc	nc	c
$Cu(AA)_2^{(pi)}$	sc	c	c
$Cu(HQ)_2^{(pi)}$	nc	nc	nc
$Cu-I^{(pi)}$	nc	sc	c
$Cu-3^{(pi)}$	nc	nc	nc
Control	nc	nc	nc

$\overline{(pi)}$ = partially insoluble; c = cured; sc = soft cure; nc = no cure

the required potlife necessitates much lower catalyst concentration and the danger of catalyst decomposition is strongly increased.

  b. Propellant

  Two propellant cure tests were conducted. The first utilized a PPG binder containing 60% AP and 20% Al in which only few catalysts effected cure. The second was a HTPB (R-45) binder with the same solids content in which all propellants, including the uncatalyzed control propellant cured.

  The propellant batch size was 100g to which were added 10 and 50 mg catalyst, respectively. All individual propellants were made from the same master batch and cure was conducted at room temperature. The results of these tests are shown in Table 40. The factors which appear to be operative in causing cure failures in the PPG propellants appear to be low catalytic activity and/or low solubility of catalysts (Fe(DAc)) and catalyst instability (Mn^{3+} catalysts).

  Further tests using other propellants with low solubility of water in the binders as well as using glass beads as a filler indicated that the culprit in all cases is most likely water. Cure failure simply boils down to the following fact: If significant quantities of water are present, only those propellants in which the urethane reaction is faster than the water-isocyanate reaction stand a chance of curing. PBD binders with their infinitesimal solubility for water usually are free of this disadvantage. AP aggravates the situation by reducing catalytic activity and introducing additional water. AP by itself appears not to accelerate or otherwise cause NCO consumption. The effects of AP on cure and homopolymerization are shown in Tables 41 and 42.

TABLE 40

AMBIENT TEMPERATURE CURE OF PROPELLANT WITH VARIOUS
FERRIC OR MANGANIC CHELATES

	PPG Propellant				HTPB Propellant	
	10 mg Catalyst		50 mg Catalyst		10 mg Catalyst	
	16 hrs	5 days	16 hrs	3 days	16 hrs	7 days
$Fe(AA)_3$	sc	c	c	c	c	c
$Fe(F_3AA)_3$	c	c	c	c	c	c
$Fe(F_6AA)_3$	nc	nc	nc	nc	sc	c
$Fe(\emptyset AA)_3$	nc	sc	sc	c	c	c
$Fe(\emptyset_2AA)_3$	nc	c	c	c	c	c
$Fe(TAM)_3$	sc	c	c	c	c	c
$Fe(DAc)_3$	nc	nc	nc	nc	sc	c
$Fe(HQ)_3$	nc	nc	nc	nc	vsc	c
$Fe(Octoate)_3$	nc	nc	nc	nc	sc	c
$Fe(o-Formylphenolate)_3$	nc	nc	nc	nc	vsc	c
$Mn(AA)_3$	nc	nc	nc	sc	c	c
$Mn(\emptyset_2AA)_3$	nc	nc	nc	nc	sc	c
$Mn(DAc)_3$	nc	nc	nc	nc	nc	c
$Mn(HQ)_3$	nc	nc	nc	nc	nc	c
$Cr(HQ)_3$	nc	nc	nc	nc	nc	c
Control (no catalyst)	nc	nc	nc	-	nc	c

c = cured

sc = soft cure

vsc = very soft cure

TABLE 41

EFFECT OF BINDER TYPE AND FILLER* ON AMBIENT CURE OF PROPELLANTS 80% b.w.

Catalyst 0.05%

Binder: B-2000/P-163/HDI 67.85/25/7.15

| | As Received Oxidizer | | Dried Oxidizer | Glass Beads |
	1 day	5 days	5 days	5 days
$Fe(AA)_3$	c	c	c	c
$Fe(\emptyset AA)_3$	sc	c	c	c
$Fe(\emptyset_2 AA)_3$	sc	c	c	c
$Fe(DAc)$	nc	sc	c	c
$Mn(AA)_3$	c	c	c	c
$Mn(HQ)_3$	nc	sc	c	c

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* The effects introduced by the AP are relatively minor compared
to the binders ability to dissolve water, which appears to be the most
important single factor affecting cure. Even comparatively wet AP still
yields cured propellants with HTPB,   while great cure difficulties
are encountered in polyethers, particularly the PPG type. This would indicate
that water dissolved in the binder phase is the actual culprit.

TABLE 42

HOMOPOLYMERIZATION OF HDI DURING 10 DAYS AT ROOM TEMPERATURE
IN THE PRESENCE OF DISSOLVED AP[*]

Solution: 10% HDI in acetone containing 1% dissolved AP and
0.2% catalyst

	NCO Remaining, Percent	
	Acetone Only	Acetone + AP
Control	100	100
Fe(AA)$_3$	83	86
Fe(F$_3$AA)$_3$	81	88
Fe(ØAA)$_3$	86	90
Fe(Ø$_2$AA)$_3$	85	91
Fe(DAc)$_3$	84	78
Mn(AA)$_3$	72	79
Mn(Ø$_2$AA)$_3$	74	82
Mn(HQ)$_3$	83	90
Mn(DAc)$_3$	79	93
Cu(AA)$_3$	22	62

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*   As found previously, AP does not add to the NCO

consumption, and, in fact, it suppresses homopolymerization.

That homopolymerization cannot be a significant factor

in cure failure is also borne out by the fact that all

HTPB propellants eventually cured.

Some 85% solids propellants were made using various
catalysts and an R-45/IDP/HDI/TEPAN bonding agent binder with 70% oxidizer
and 15% aluminum powder. The mechanical properties of the ambient tempera-
ture cured propellants utilizing some representative catalysts are shown in
Table 43. The effect of TEPAN on mechanical properties can be ascertained
by comparison with one of the one pound batches not containing the bonding
agent. Except for Fe(DAc)$_3$ and Mn(HQ)$_3$ none of the catalyzed one pound
propellants had a potlife exceeding 4 hrs at room temperature. The 4000g
(nominal 10-1b) batches differ from one pounders by substitution of distilled
HDI with "as received" HDI and a lower catalyst concentration. The ambient
cure time for these propellants was 3 days less. It is noteworthy that the
Fe($\emptyset_2$AA)$_3$ catalyzed 10-1b batch cured faster and harder than Fe(AA)$_3$, prob-
ably because at these very low catalyst concentrations, decomposition of
the catalyst has a noticeable effect and because Fe($\emptyset_2$AA)$_3$ is more stable
than Fe(AA)$_3$. After the indicated time at ambient temperature, the pro-
pellants were subjected to an additional 3 days at 135°F to ascertain to
what extent the ambient cure was complete.

It is important to note, that the control propellant
for the 400g batches had a lower modulus and tensile strength than the
catalyzed propellants with the exception of Mn(HQ)$_3$ and, of course, the
propellant not containing the bonding agent. In fact, the level of cure
reached depends strongly on the rate of cure. It therefore appears to be
a fallacy if we assume that slower catalysts will eventually yield the same
level of cure (modulus, tensile strength) as the more efficient catalysts.
This is also borne out by the data of the 10 pound batches. Its explanation
is simply that during slower cure, cure side reactions have a greater
effect on the overall state of cure.

All propellants containing the manganic catalyst
yielded a dry, crumbly propellant surface. This fact and their poor
performance in homopolymerization and stability tests make them less
desirable candidates unless these drawbacks can be overcome.

TABLE 43

MECHANICAL PROPERTIES OF HTPB PROPELLANTS AFTER 10 DAYS OF
AMBIENT CURE AND AFTER ADDITIONAL 3 DAYS AT 135°F

Latter values in parentheses

400g Batches - Catalyst Concentration 0.005%

	σ_{max}	ϵ_{max}	E_o
$Fe(AA)_3$	135	28	600
	(149)	(31)	(611)
$Fe(\emptyset_2AA)_3$	140	32	572
	(139)	(30)	(587)
$Fe(F_3AA)_3$	143	31	528
	(155)	(35)	(550)
$Fe(DAc)_3$	125	35	497
	(135)	(32)	(607)
$Mn(HQ)_3$	84	23	477
	(94)	(26)	(523)
T-12	125	32	455
	(130)	(41)	(407)
Control	115	37	462
	(104)	(44)	(370)
$Fe(AA)_3$, no TEPAN	66	34	242
	(81)	(29)	(336)

4000g Batches (7 day ambient cure) - Catalyst Concentration 0.0012%

	σ_{max}	ϵ_{max}	E_o	Rex Hardness		
				4 hrs	20 hrs	5 days
$Fe(AA)_3$	98	41	292	s	60	60
	(110)	(36)	(402)			
$Fe(\emptyset_2(AA)_3$	117	31	451	50	60	60
	(128)	(32)	(539)			
$Fe(DAc)_3$	83	44	204	s	30	50
	(91)	(39)	(310)			
$Mn(HQ)_3$	88	40	281	s	s	35
	(89)	(43)	(275)			

s = too soft to measure

7.   A New Type of Ferric Catalysts

During the later stages of the program it was discovered that combination of solutions of $FeCl_3$ and $Fe(AA)_3$ showed a minimum activity at a composition corresponding to $Fe(AA)_2Cl$. Simultaneously a solubility minimum allowing isolation of the compound was obtained. The same test carried out with combinations of solutions of ferric octoate and $Fe(AA)_3$ gave a maximum activity at $Fe(AA)_2OOCC_7H_{15}$. The rates were obtained by the exotherm method in butanol and are shown in Table 44. It is, however, possible to isolate only the compounds made with strong acids. If the radical of a weak acid replaces one acetylacetonate ligand, attempts to isolate the compound failed, but their presence can be established in solution. Thus $Fe(AA)_3-Fe(OOCC_7H_{15})_3$ shows an activity maximum at a composition of the mixture corresponding to $Fe(AA)_2(OOCC_7H_{15})$ (Table 44). Since these compounds may be valuable catalysts a total of seven were prepared by the modification of $Fe(AA)_3$. The methods of preparation sought to use one of the two following general reactions to accomplish the indicated change.

$$(1) \quad Fe(AA)_3 + HX = Fe(AA)_2X + HAA$$

$$(2) \quad 2Fe(AA)_3 + FeX_3 = 3Fe(AA)_2X$$
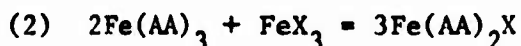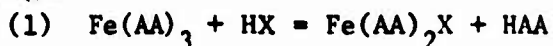
The proportions reacted are shown in Table 45.

The free acids used were p-toluenesulphonic acid monohydrate, benzilic acid, chloroacetic acid, o-cresol, 8-hydroxyquinoline, and mandelic acid. $Fe(AA)_3$ and an appropriate amount of HX were mixed and dissolved in xylene. The solution was heated to remove about half of the xylene and to carry off the HAA produced. Hexane was added to precipitate the product. The product was filtered, washed, and dried before use. No chemical analyses were made, but the DSC thermogram was determined.

Only $Fe(ClO_4)_3 \cdot 6H_2O$ and $FeCl_3$ were available to produce compounds according to reaction 2. A benzene solution containing appropriate

TABLE 44

RELATIVE CATALYTIC EFFICIENCY OF $FeCl_3-Fe(AA)_3$ AND $Fe(OCTOATE)_3 - Fe(AA)_3$
MIXTURES IN THE REACTION BETWEEN METHANOL AND HDI AT 25°C

Molar Ratio of Catalyst	Relative Rate of $FeCl_3/Fe(AA)_3$ System	Relative Rate of Fe Octoate/$Fe(AA)_3$ System
10/0	1.47	0.105
9/1	1.28	0.29
8/2	1.04	0.56
7/3	0.71	0.72
6/4	0.47	1.02
5/5	0.33	1.14
4/6	0.25	1.32
3/7	0.24	1.46
2/8	0.40	1.38
1/9	0.52	1.34
0/10	1.00	1.00

TABLE 45

REACTION PROPORTIONS AND DSC DATA FOR MODIFIED Fe(AA)$_3$ CATALYSTS

Compounds	1	2	3	4	5	6	7
Fe(AA)$_3$	3.33	4.5	3.66	5.08	4.89	4.34	4.36
Fe(ClO$_4$)$_3$·6H$_2$O	2.18	-	-	-	-	-	-
CH$_3$C$_6$H$_4$SO$_3$H·H$_2$O	-	2.24	-	-	-	-	-
(C$_6$H$_5$)$_2$CHOHCOOH	-	-	2.37	-	-	-	-
CH$_2$ClCOOH	-	-	-	1.36	-	-	-
CH$_3$C$_6$H$_4$OH	-	-	-	-	1.50	-	-
C$_7$H$_6$NOH	-	-	-	-	-	1.82	-
C$_6$H$_5$CHOHCOOH	-	-	-	-	-	-	1.89
DSC Data							
Endotherms, °C	109	168	170	-	187[b]	170[c], 227	-
Exotherms, °C	-	-	-[a]	185	-	-	-

[a]Exotherm immediately after endotherm
[b]No depression with Fe(AA)$_3$
[c]Same endotherm occurs in mixture with Fe(AA)$_3$

amounts of the FeX_3 and $Fe(AA)_3$ was evaporated on a hot plate to remove water. Then hexane was added and the compound formed isolated as above.

DSC thermograms were obtained with from 3-9 mg of material at a heating rate of 10 or $20°K/min$. The data are reported in Table 45.

Some of these compounds have been used in propellants. The results obtained will be discussed later.

E.   CONTROL OF CATALYTIC ACTIVITY

1.   General Considerations

All observations presented thus far indicate that it may not
be possible to find a catalyst which catalyzes the urethane reaction only.
Even if such a catalyst could be found it might not be possible to eliminate
side reactions which also occur in the uncatalyzed propellant and are not
influenced by the catalyst. To illustrate this point, suppose a catalyst is
available which only accelerates the alcohol-isocyanate reaction. The usually
required potlife of 8 hours requires reduction of catalyst activity to a point
where these uncatalyzed reactions become significant, the severity, of course,
depending on the level of impurities. Therefore, practical polyurethane propel-
lants cannot be expected to reach the same state of cure (hardness), if the
duration of cure is varied by changes of catalyst level or temperature or both.
Slower curing propellants will always be softer. The most important interference
reactions are probably caused by moisture and the self condensation (homopoly-
merization) of NCO groups. Allophanate and biuret condensations are probably
less significant. The effect of nonGaussian chain lengths distribution may
also be of importance here, but its magnitude must yet be established. Not all
of these reactions are affected by the specific polymerization catalyst and
exhibit a different temperature dependence of reaction rate. Thus, the water-
isocyanate reaction is more serious at low temperatures, where it consumes a
larger proportion of isocyanate groups, than at higher temperatures, where the
urethane reaction is favored.

A good catalyst accelerates the urethane reaction, i.e., the
cure reaction proper, leaving side reactions comparatively unaffected to proceed
essentially at the same rate as in the absence of the catalyst. At higher levels
of catalyst, therefore, the effects of side reactions are minimized and the
overall state of cure and hence reproducibility as well as mechanical properties
are improved.

The level of contaminants (moisture, etc.) in propellants may
vary, depending on exposure to the environment and the characteristics of the
propellant components which may not be known with the desired precision. While

some of the contaminants may be neutralized by suitable scavengers, it is obviously good practice to minimize the cure time during which these substances can interfere with the urethane reaction. This cure time, unfortunately, must include a lengthy period, referred to as potlife (usually about 8 hours are required) during which the propellant batch must remain liquid in order to be cast into motor chambers. During this time, the propellant viscosity at all shear levels should not rise above 50,000 poise, to assure flaw-free castings.

HTPB prepolymers have about the highest reactivity of any hydroxyl containing compound. Thus, in order to obtain the desired potlife the slower reacting isocyanates such as TDI, HDI, IPDI, etc. must be used. Aromatic isocyanates with unhindered NCO groups, or, even more so, electronegatively substituted isocyanates such as tetrafluoro-1,4-phenylene diisocyanate, are too fast, even uncatalyzed, to be applicable.

Even less reactive isocyanates, require low concentrations of the more effective catalysts or the propellant potlife is undesirably short. Slightly higher concentrations of moderately active catalysts can be used. However, the catalysts which are best in promoting the urethane reaction are also the most active ones so that only very small catalyst concentrations are permissible. This poses an additional problem in that at low concentrations, the catalyst can be completely lost by hydrolysis or other degradative reactions. One method which has been quite successful was the modification (weakening) of catalyst activity by the simultaneous addition of a chelating agent, usually the same that is contained in the metal chelate catalyst, e.g. the combination $Fe(AA)_3$-HAA[22]. With this modification the catalyst concentration can be increased to safe levels and, moreover, the free chelating agent acts as a stabilizer for the catalyst further reducing the danger of loss by degradative reactions.

While the $Fe(AA)_3$-HAA method has worked satisfactorily in many applications, the over-all required cure times are moderately long and may give contaminants too much opportunity to interfere. Therefore, emphasis was placed

on methods which shorten the overall cure time without sacrificing potlife,
i.e. trying to obtain differential catalytic activity which is very low at
the initial stages of cure but increases rapidly with time. The methods designed
and investigated to achieve this goal can be classified as:

Catalysis by controlled diffusion,

Formation of catalyst in curing propellant, and the

Catalyst-suppressor-scavenger method.

2. Catalysis by Controlled Diffusion

The basic idea in this approach is that a suitable catalyst,
e.g. $Fe(AA)_3$, must diffuse out of a polymer in which it has been occluded in order
to become active. This diffusion process takes time and, therefore, provides
the desired potlife. With time, the concentration of catalyst increases in the
uncured propellant with a concomitant increase in the rate of cure. Several
factors will influence the quantity of diffusing catalyst.

These are:

a. Concentration of catalyst in particle

b. Molecular weight of catalyst

c. Relative solubility of catalyst in encapsulating
    material and in the propellant binder matrix

d. Modulus of encapsulating material (an important
    factor since swelling precedes extraction)

e. Size of the particles containing the catalyst.

To illustrate point c. above: Five percent of $Fe(AA)_3$ were
incorporated into a binder consisting of a stoichiometric mixture of (a) R-45M/
TDI and (b) TP-440/TDI. TP-440 is a PPG type triol with an equivalent weight of
140. The resulting materials were shredded and 0.2g of each was suspended in
20 cc of either isodecyl pelargonate or dimethyl phthalate plasticizer. The
suspension was stirred overnight and the concentration of $Fe(AA)_3$ dissolved in
the plasticizer was determined with a Beckman spectrophotomer. IDP extracted
only about 2% of the $Fe(AA)_3$ from the TP-440 resin, while DMP extracted about
62% of the available $Fe(AA)_3$. From the R-45M/TDI polymer, IDP extracted 52%
$Fe(AA)_3$ and DMP 83% $Fe(AA)_3$. This difference of extractability was supported by

cure tests. The R45M/TDI polymer yielded very fast cures, when used at the 0.2% level, whereas the TP-440/TDI polymer cured more slowly. Only a small fraction of the $Fe(AA)_3$ contained in the TP-440 polymer is utilized if it is used in IDP plasticized HTPB binder systems. An improvement in the $Fe(AA)_3$ diffusion efficiency is achieved if the polymeric encapsulating material is plasticized. Polymers filled with $Fe(AA)_3$ at 3, 5, 7.5 and 10% by weight and also plasticized at the 10, 30 and 50% level with DMP or IDP were made from R-45M/TDI or HDI, GTRO/TDI or HDI, TP-340/TDI and TP-440/TDI. By choosing the proper particle size all of these polymers yielded a satisfactory ratio of potlife to cure time. The difficulty experienced here was the grinding of the cured polymer to the desired particle size. The very hard polymers must be ground finer than the softer GTRO or R-45M polymers. Waring blenders are not suitable because after the particle has reached a certain size, it is bounced around by the blades without further decrease in size. In addition, the yield of material of the proper particle size is very low.

To overcome this disadvantage, an emulsion polymerization technique was developed and spherical particles containing the $Fe(AA)_3$ catalyst were prepared in sizes ranging from less than 100 to over 2000μ. The most significant factor affecting particle size is the choice and quantity of the wetting agent. Temperature and rate of stirring are comparatively insignificant. Figure 26 shows photomicrographs at 40X magnification of some $Fe(AA)_3$ containing GTRO/HDI polymers plasticized with 30% DMP and prepared in aqueous suspension at 120°F. Most of the $Fe(AA)_3$ is trapped by the polymer, as found by subsequent analysis. The $Fe(AA)_3$ at these high concentrations is not dissolved in the polymer as the dark areas inside the spheres (Figure 26) indicate. High concentrations of $Fe(AA)_3$ were found to require significantly increased quantities of wetting agent.

In a typical preparation, about 50g of a mixture of glycerol tririncinoleate, dimethyl phthalate and $Fe(AA)_3$ is poured into a 120°F warm, stirred solution of 500ml water containing 1g lecithin. To this stirred mixture 130 eq.% of HDI are added over a period of 30 seconds. Polymerization takes place within 10 to 12 min; the average particle size of the resulting spheres

Fe(AA)$_3$ OCCLUDED IN EMULSION POLYMERIZED
POLYURETHANE ELASTOMER PARTICLES
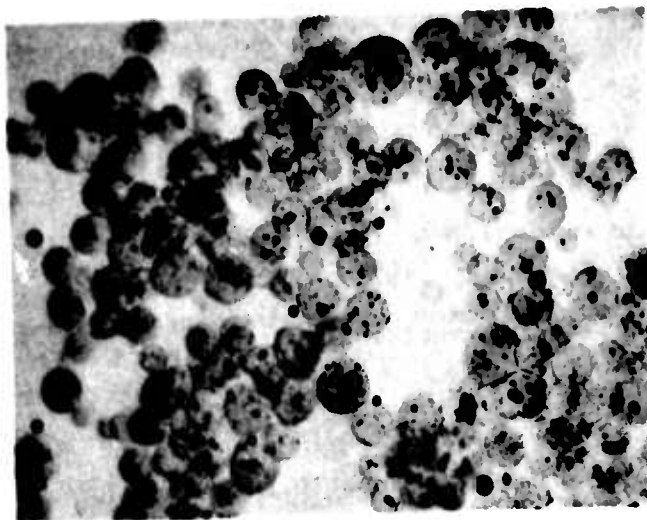
5% Fe(AA)$_3$; 1g Lecithin

5% Fe(AA)$_3$, 1g C$_{11}$H$_{23}$SO$_4$Na   20% Fe(AA)$_3$, 1g Lecithin
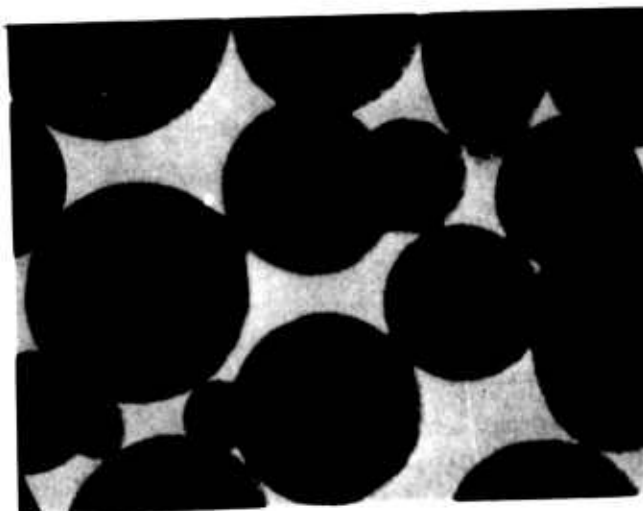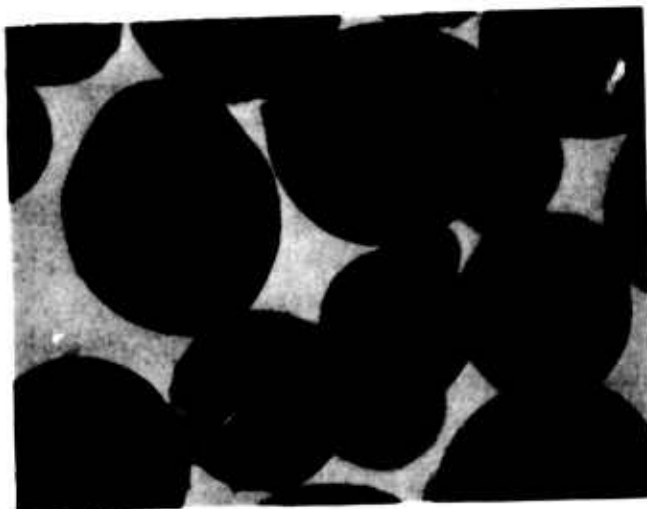
Figure 26

is about 250μ. After completion of polymerization, the spheres are washed
several times with water to which a few drops of Lux (liquid household
detergent) are added. The latter treatment prevents agglomeration of the
polyurethane spheres as the wetting agent is washed out. Finally, the material
is filtered and dried in air. Polymerization conducted at temperatures higher
than 120°F is not recommended as larger quantities of the $Fe(AA)_3$ are hydrolyzed.
Cure time and the quantity of $Fe(AA)_3$ retained in the particles at different
polymerization temperatures are listed in Table 46 for the above recipe.

TABLE 46

EFFECT OF TEMPERATURE OF POLYMERIZATION ON CURE TIME AND $Fe(AA)_3$ RETENTION IN A GTRO/DMP/HDI POLYMER

Temperature, °F	Cure Time (min)	% $Fe(AA)_3$ Retained
Ambient	90	73
100	40	69
120	12	65
148	8	42

The percentage of retained $Fe(AA)_3$ increases with increasing $Fe(AA)_3$ concen-
tration. For example, when 10 and 20% $Fe(AA)_3$ were used, retention at 120°F
polymerization was 86 and 93%, respectively.

Only lecithin, sodium lauryl sulfate and Lux were tested as
wetting agents. Each of these materials was effective with minor adjustments
in concentration. Other prepolymers such as R-45M, polyesters and other water
insoluble prepolymers can also be used to form the polymer matrix. The applied
isocyanate should be in excess, at least 20%, preferably 30-40%, since consid-
erable quantities of water also react.

A detailed study has shown that the mechanical properties of
the propellants made with encapsulated catalysts are inferior to those obtained
with the free catalyst. Table 47 shows some of the results obtained with an
HTPB type propellant system containing 85 wt% solids, and various quantities

TABLE 47

MECHANICAL PROPERTIES OF HTPB PROPELLANT, 85% BY WEIGHT SOLIDS,
MADE WITH ENCAPSULATED AND FREE $Fe(AA)_3$
(Propellant Cured 7 Days at Ambient Temperature)

Catalyst, %		Mechanical Properties at $+77°F$ [c]		
		σ_m, psi	ε_m, %	E_o, psi
Encapsulated				
$Fe(AA)_3$ [a]	0.025	41	37	132
"	0.050	57	34	198
"	0.100	67	38	215
"	0.200	105	43	330
Free $Fe(AA)_3$	0.001 [b]	82	48	255
"		115	37	370
"		128	42	430

(a) Concentration shown includes polymer which contained 3.5% $Fe(AA)_3$.
(b) Modulus adjusted by varying level of diisocyanate.
(c) $\dot{\varepsilon} = 0.74$ min^{-1}.

of an encapsulated catalyst (5% Fe(AA)$_3$ in the GTRO/DMP/HDI polymer of approximately 300µ average particle size). For comparative purposes the propellant formulation containing the free FeAA was cured to different hardnesses by adjusting the level of the diisocyanate. Data from Table 47 show that the properties obtained with the encapsulated catalyst are less satisfactory than those obtained with unencapsulated Fe(AA)$_3$, at least for the allotted duration of cure. At comparable moduli the tensile strength as well as elongation of the propellants using Fe(AA)$_3$ in its free form are significantly better. This is probably due to gradation in catalyst concentration in the binder matrix, when catalyst diffusion is used to control potlife. Where the catalyst concentration is high, the propellant modulus is higher than in those areas where the catalyst concentration is lower. In the areas of low catalyst concentration isocyanate consuming side reactions may also become relatively more serious.

Consequently, around the spheres containing the catalyst the propellant cures harder than farther away in the matrix. If such a propellant specimen is subjected to stress, the harder domains will yield less than the softer ones. Since the stress at which cohesive failure occurs depends directly on the elastic modulus of the material,[23] failure will initiate in these areas before the harder domains have contributed much to the overall deformation. The net effect is that the applied stress is borne by only a fraction of the propellant matrix, which in turn, results in early failure. Table 47 shows that with increasing concentration of the encapsulated catalyst the properties improve significantly. If very small spherical particles were used, this deleterious effect on mechanical properties could be brought to a minimum, but would defeat the purpose of a diffusion controlled slow cure.

It appears that high temperature aging of these propellants greatly improves the mechanical properties. It is possible that the higher temperature drives the cure to completion and thus improves mechanical properties. However, the use of high temperature cure is contrary to the objectives of this program. Table 48 shows 1 month, 160°F aging results obtained with propellants which were catalyzed with Fe(AA)$_3$ occluded in polyurethane spheres.

TABLE 48

EFFECT OF 160°F AGING (1 MONTH) ON MECHANICAL PROPERTIES
OF R-45M-IDP-HDI PROPELLANTS CATALYZED WITH
$Fe(AA)_3$ OCCLUDED IN POLYURETHANE SPHERES

% FeAA Occluded	Mechanical Properties at +77°F [*]					
	Initial			Aged		
	σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi
0.02	91	37	312	172	33	664
0.005	100	31	385	152	32	600

[*] $\dot{\epsilon} = 0.74$ min^{-1}

3. Formation of Polymerization Catalyst During Cure

In this approach the catalyst for the urethane reaction is
formed in the propellant medium. Examples are

$$ZnO + 2HAA \longrightarrow Zn(AA)_2 + H_2O,$$

$$ZnO + 2RCOOH \longrightarrow Zn(OOCR)_2 + H_2O.$$
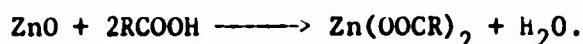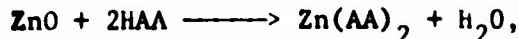
In such a system the rate of cure is very slow during the initial stages but
speeds up enormously as the acetylacetone is consumed. In this manner the dual
effect of increasing catalyst concentration and decreasing suppressor concen-
tration is obtained. To date, all attempts to use ferric compounds in this
approach have been unsuccessful. Only ZnO which converts to $Zn(AA)_2$ by HAA
or PbO produced cure. Lead oxide, furthermore, is only converted into a chelate
by the more acidic diketones, notably hexafluoroacetylacetone. Much faster
conversions are achieved with acids, of which p-toluenesulfonic acid, linoleic
acid and α-bromotetradecanoic acid were tried. All of these increased the rate
of cure. ZnO and PbO were employed as metal donors. Propellants were prepared
using either HDI (Table 49) or TDI as curative (Table 50).

In the slower curing Li initiated prepolymers this cure system
has not been successful, even when elevated cure temperatures (135°F) were
employed. Cure was very sluggish and also appeared to require a larger pro-
portion of isocyanate. The reason for this behavior is probably that the zinc
catalyst is not specific for the urethane reaction. In R-45M propellants,

TABLE 49

MECHANICAL PROPERTIES OF R45M/HDI HTPB PROPELLANT CONTAINING 85 WT% SOLIDS
(Catalyst formed during cure)

Catalyst System	Uniaxial Tensile Properties at 77°F[a]					
	7 days cure r.t.			7 days r.t. + 48 hrs 180°F		
	σ_m psi	ϵ_m %	E_o psi	σ_m psi	ϵ_m %	E_o psi
ZnO 0.1%, linoleic acid 0.008%	121	40	420	123	48	395
ZnO 0.1%, α-bromotetradecanoic acid 0.08%	110	35	396	120	42	387
ZnO 0.1%, p-toluenesulfonic acid 0.04%	115	41	418	121	43	415

[a] Standard JANAF tensile specimen. $\dot{\epsilon}$ = 0.74 min^{-1}

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TABLE 50

MECHANICAL PROPERTIES OF R45M/TDI PROPELLANTS CONTAINING 88WT% SOLIDS

Catalyst Formed During Cure

| | Uniaxial Tensile Properties @ 77°F[a] | | | | | | |
| | 7 days r.t. cure | | | 2 wks 1$\dot{0}$0°F | | | |
Catalyst System	σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi
ZuO 0.1%, linoleic acid 0.5 mmole [b]	144	27	800	167	30	820
PbO 0.1%, linoleic acid 0.5 mmole	151	24	910	170	21	1050
Control, no catalyst	98	30	550	143	24	790

[a] Standard JANNAF tensile specimen. $\dot{\epsilon} = 0.74$ min^{-1}

[b] mmoles – millimoles per 400g propellant.

owing to the large excess of hydroxyl groups over the NCO groups these side reactions are minimized, but in stoichiometrically cured Li HTPB, side reactions become appreciable during the last stages of cure, because the concentration of cure interfering impurities becomes significant compared to the concentration of hydroxyl groups.

For Li HTPB systems, only p-toluenesulfonic acid in combination with ZnO resulted in a cured propellant but three weeks at ambient were required to promote a soft cure. Moreover, the exposed propellant surfaces showed extensive decomposition, probably, a result of moisture interference reactions, which depleted the NCO content and resulted in poor cure.

Very little success was achieved with ferric compounds used as metal donors. Even with acids they hardly reacted. The ferric compounds tried were Fe_2O_3, freshly prepared $FeO(OH)$, and a polymeric ferric carbonate.

Use of diketones instead of acids resulted in more sluggish cures. These systems may be useful at elevated cure temperatures, where the lower reactivity of the diketones is somewhat offset. The chelating agents tested were 1,4-pentanedione (HAA), 1,3-diphenyl-1,3-propanedione (ϕ_2AAH), triacetylmethane (HTAM), 8-hydroxyquinoline (HQ), 1,1,1-trifluoro-2,4-pentanedione (F_3AAH), 1,1,1,5,5,5-hexfluoro-2,4-pentanedione (F_6AAH), 1-phenyl-1,3-butanedione (ϕAAH), and dehydroacetic acid (HDAc).

The above materials were evaluated by adding 0.2% by weight of the ferric compound and about 50mg of the chelating agent to an R-45M/IDP/HDI binder containing 80% by weight of NH_4ClO_4. None of these combinations cured significantly faster than the uncatalyzed control. Obviously, the rate of conversion to the ferric chelate with the iron compounds is too slow under ambient temperature conditions. In some cases, as with $Fe_2(SO_4)_3$, a definite color change to the corresponding ferric chelate was observed although cure was hardly affected. Even when subjected to elevated temperatures cure was not significantly different from uncatalyzed propellant controls.

Zinc oxide proved to be the best performer with diketones as well. $Zn(AA)_2$ is a good urethane catalyst in the absence of moisture. It can, therefore, be used in HTPB propellants where the moisture content is low. By contrast,

$Zn(AA)_2$ is unsuitable in polyether prepolymers where the moisture content is high.

The ZnO-HAA system works best at slightly elevated temperatures. Table 51 shows the properties obtained with an 85 wt% solids R-45M/IDP/TDI/TEPAN binder system cured 4 days at 110°F. A 10 day cure at ambient temperature was also conducted on a 10-lb propellant batch.

The data in Table 51 indicate that the ZnO-HAA system might very well be a feasible catalytic system, although not as versatile as the $Fe(AA)_3$-HAA-ZnO method described later. Due to the total absence of catalytic activity during the initial stages of cure, this method of catalysis undoubtedly yields the best propellant potlife. An advantage of this system is the use of ZnO and PbO in place of iron compounds which will greatly reduce the danger of oxidative crosslinking of double bonds. The latter is adversely affected by transition metal ions, including the ferric ion.

4. Catalyst-Suppressor-Scavenger Method

The catalytic activity of most metal catalysts can be greatly reduced if a chelating gent is added to the system. Figure 1 and Table 52 shows this effect for a few catalyst-chelate agent combinations. It is not important that the chelating agent be the same as that in the parent catalyst.

The $Fe(AA)_3$/HAA combination has been used widely to improve the potlife of propellants because it provides a catalyst of lower activity without resorting to a different metal ion with potentially less favorable over-all characteristics. Like any method, the $Fe(AA)_3$/HAA method has its limitations. One of these is the increased frequency of soft center cure if the weight ratio of $Fe(AA)_3$/HAA becomes less than unity. Soft center cure is characterized by an uncured interior accompanied by an apparently well cured outer crust. In order to obtain sufficient potlife in many HTPB propellant systems, the $Fe(AA)_3$/HAA ratio has to be considerably less than unity. This, of course, extends the cure time. The idea followed here was to add a substance to the catalyst-chelating agent combination which would slowly consume the chelating agent thus restoring the activity of the catalyst. This approach is akin to the initially followed attempt

TABLE 51

FORMATION OF Zn CATALYST IN PROPELLANT DURING CURE

Propellant	ZnO, %*	HAA*	HF$_6$AA*	Cure Time, Days	Mechanical Properties at +77°F**		
					σ_m, psi	ϵ_m, %	E_o, psi
1	0.1	0.025	-	4	180	30	840
2	0.1	-	0.025	4	189	28	950
3	0.2	-	0.05	4	188	26	1000
4***	0.1	0.025	-	10	82	54	220

* Concentration based on propellant

** $\dot{\epsilon}$ = 0.74 in./in./min. The high moduli, coupled with high tensile and low elongation are primarily due to an excess of the TDI curing agent.

***Ten-lb batch cured at ambient temperature.

TABLE 52

EFFECT OF CHELATING AGENTS ON RELATIVE RATE OF THE CATALYZED
METHANOL-HDI REACTION AT 25°C

Catalyst Concentration 0.2%

Catalyst	Chelating Agent, %	Relative Rate
Fe(AA)$_3$	None	1
	HAA, 0.01	0.50
	HAA, 0.025	0.25
	HAA, 0.050	0.19
	HAA, 0.100	0.065
	Hϕ_2AA, 0.05	0.35
	Hϕ_2AA, 0.1	0.19
	Hϕ_2AA, 0.2	0.11
	Hϕ_2AA, 0.4	0.04
	HAA, 0.1	0.065
	Hϕ_2AA, 0.1	0.19
	HF$_3$AA, 0.1	0.06
	HF$_6$AA, 0.1	0.05
	HDAc, 0.1	0.11
	HTAM, 0.1	0.24
	HBAA, 0.1	0.12
Fe(ClO$_4$)$_3$	None	1.0
	HAA, 0.01	0.71
	HAA, 0.025	0.40
	HAA, 0.05	0.36
Zn(AA)$_2$	None	1.0
	HAA, 0.01	0.30
	HAA, 0.025	0.14
	HAA, 0.050	0.09
	HAA, 0.10	0.04
T-12	None	1.0
	HAA, 0.10	0.68
	HAA, 0.40	0.29
	HAA, 1.00	0.13

Legend: HAA = 2,4pentanedione   HDAc = Dehydracetic acid
         Hϕ_2AA = Dilenzoylmethane   HTAM = Triacetylmethane
         HF$_3$AA = Trifluoroacetylacetone   HBAA = 3-Benzoylacetylacetone
         HF$_6$AA = Hexafluoroacetylacetone   T-12 = Dibutyltin dilaurate

of creating the catalyst in situ, e.g., by the metathesis of the chelating
agent with ferric oxide or the like. The present approach, although appearing
more complex, has the advantage that a large variety of compounds can be
used as scavengers for HAA, while only very few metal compounds can be con-
verted into useful catalysts. Another advantage of this method is its flex-
ibility. For example in many highly thixotropic propellants, the batch fluidity
can be greatly improved if some of the hydroxyl groups are reacted with the
diisocyanate. The latter reaction reduces hydrogen bonding between OH groups
which is probably responsible for the dry stage observed before isocyanate
addition. This initial reaction can be accomplished simply by introducing
the catalyst prior to the HAA. When the batch fluidity is optimum, further
reaction is retarded by adding the chelating agent. This feature is missing
with the ZnO-HAA or ZnO-acid methods.

A large number of metal oxides and other compounds have been
tested as scavengers for HAA. Compounds that showed positive response at
ambient temperature were ZnO, $Ag_2Cr_2O_7$, $[Fe(urea)_3](ClO_4)_3$, CaO, MnO(OH), PbO
and $[Ni(en)_3]Cl_2$ (en = ethylenediamine). Ineffective compounds were $Al(OH)_3$,
MgO or $Mg(OH)_2$. Of the above compounds ZnO and $[Ni(en)_3]Cl_2$ performed best
and therefore were investigated in more detail.

a. Propellants Based on R-45M

The infinite shear viscosities of some representative
propellants made with the R-45M/IDP/HDI binder system containing 85 wt% solids
are shown in Figure 27. The properties of these propellants are listed in Table 53.
It is interesting to note that Propellants 3 and 4 took longer to cure and,
therefore, also cured somewhat softer than Propellants 5 and 6. The reason is the
higher absolute concentration of HAA which requires a longer time of scavenging.

The data in Figure 27 and Table 53 show that suitable
propellants can be prepared by this method. These propellants have a 10-12 hour
potlife (batch viscosities below 30,000 poise) and reach full cure within 2 to
3 days after batch preparation. Since different prepolymers and isocyanates
require different degrees of catalysis to obtain the desired balance between
potlife and cure time, it is also important to ascertain the optimum combination
of catalyst, suppressor and scavenger. Investigations of this sort are described
below.

VISCOSITY BUILDUP AT ROOM TEMPERATURE OF
HTPB PROPELLANTS CONTAINING 85% BY WEIGHT SOLIDS
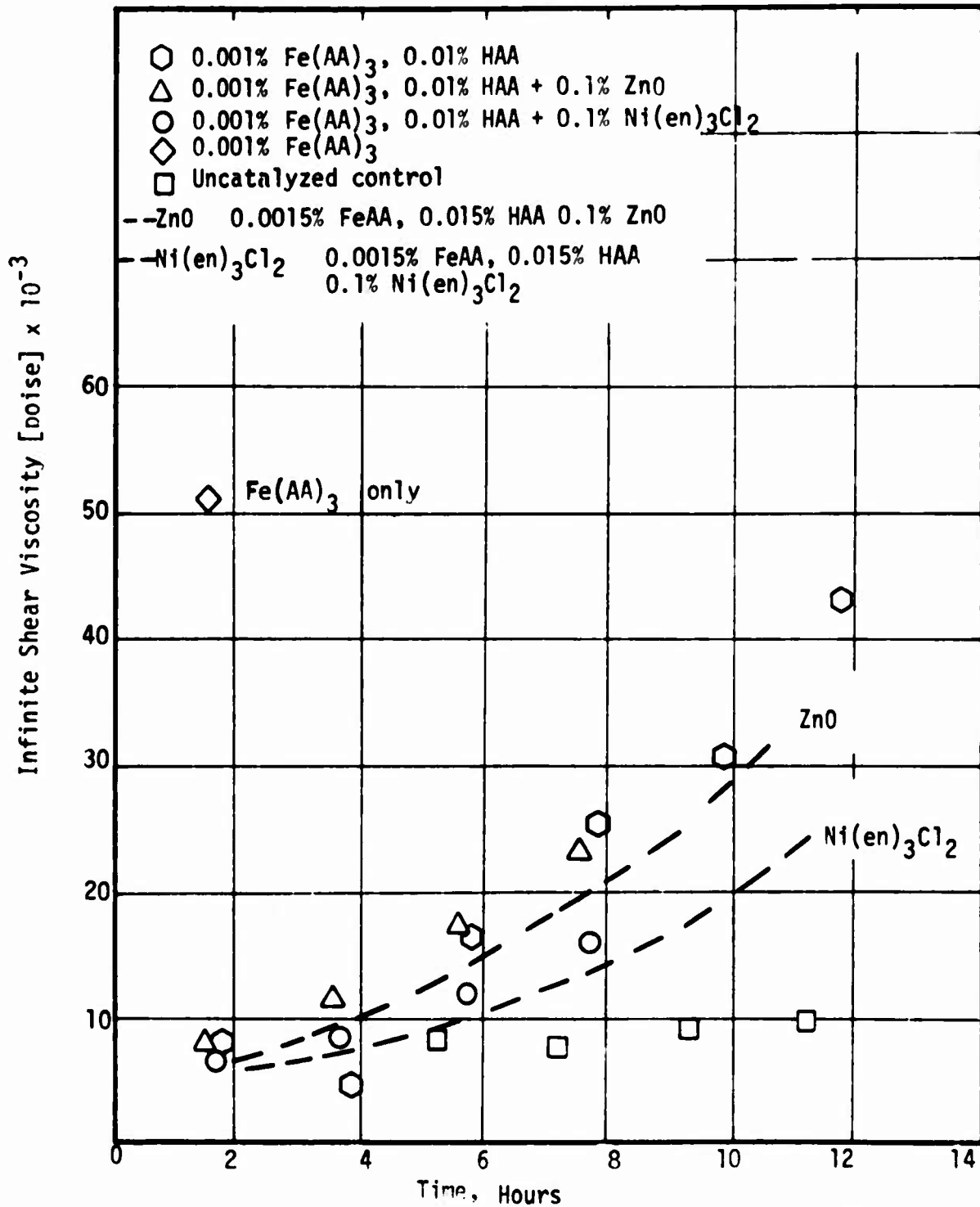
Figure 27

TABLE 53

MECHANICAL PROPERTIES OF HTPB PROPELLANTS CURED AT ROOM TEMPERATURE

No.	Catalyst Combination, %				Shore Hardness After Days Cure			Mechanical Properties at 77°F**		
	$Fe(AA)_3$	HAA	ZnO	$Ni(en)_3Cl_2$	2	3	5	σ_m psi	ϵ_m %	E_o psi
1	0.00150	0.075	0.1	-	47	47	45	127	38	457
2	0.00150	0.075	-	0.1	42	44	45	129	37	490
3	0.0015	0.015	0.1	-	37	39	40	118	38	424
4	0.0015	0.015	-	0.1	15	35	40	116	41	430
5	0.001	0.01	0.1	-	35	43	45	127	35	506
6	0.001	0.01	-	0.1	20	35	40	125	37	470
7	0.001	0.01	-	-	-	15	25	92	41	235
8	0.001*	-	-	-	40	40	40	117	37	410
9	-	-	-	-	-	-	15	65	47	135

* At these low levels of $Fe(AA)_3$ without the stabilizing effect of the chelating agent, catalyst decomposition often occurs and the final state of cure will be soft.

** $\dot{\epsilon}$ = 0.74 in./in./min.

TABLE 53 (cont.)

MECHANICAL PROPERTIES OF HTPB PROPELLANTS CURED AT ROOM TEMPERATURE

No.	Catalyst Combination, %				Shore Hardness After Days Cure			Mechanical Properties at 77°F**		
	$Fe(AA)_3$	HAA	ZnO	$Ni(en)_3Cl_2$	2	3	5	σ_m psi	ϵ_m %	E_o psi
1	0.00150	0.075	0.1	-	47	47	45	127	38	457
2	0.00150	0.075	-	0.1	42	44	45	129	37	490
3	0.0015	0.015	0.1	-	37	39	40	118	38	424
4	0.0015	0.015	-	0.1	15	35	40	116	41	430
5	0.001	0.01	0.1	-	35	43	45	127	35	506
6	0.001	0.01	-	0.1	20	35	40	125	37	470
7	0.001	0.01	-	-	-	15	25	92	41	335
8	0.001*	-	-	-	40	40	40	117	37	410
9	-	-	-	-	-	-	15	65	47	135

* At these low levels of $Fe(AA)_3$ without the stabilizing effect of the chelating agent, catalyst decomposition often occurs and the final state of cure will be soft.

** $\dot{\epsilon}$ = 0.74 in./in./min.

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It is not necessary that the chelating agent used to suppress the activity of the metal catalyst be identical with the one contained in the catalyst. For example, diphenylpropanedione can be used to suppress the catalytic efficiency of ferric acetylacetonate, etc. The use of more acidic chelating agents was of special interest since these materials potentially could obviate the need for separate scavengers. For example, hexafluoroacetyl-acetone may react with the aluminum powder in conventional propellants and thus become inactivated. Table 54 shows results obtained from screening experiments conducted on a number of chelating agents. Only commercially available compounds were tested. The test system was R-45M-IDP-HDI containing 20% Al and 60% AP. Diphenylpropanedione (ϕ_2AAH), trifluoroacetylacetone (F_3AAH), and hexafluoroacetyl-acetone (F_6AAH) are tne most reactive chelating agents of all those tested. The fluoro compounds, however, may be objectionable because of their extremely unpleasant, pungent odor and potential instability. Based on the rate of hardness increase, PbO and ZnS do not appear to be good scavengers at room temperature. Zinc oxide appears to perform satisfactorily with HAA.

Table 55 shows the results of a number of 1-1b batches made with ϕ_2AAH, and F_6AAH using an 85 wt% solids R-45M-IDP-HDI system. With the exception of the F_6AAH system, all batches cured to about the same level. $Fe(F_6AA)_3$ solutions have been observed to fade rapidly in color due to the formation of insoluble, inert, white FeF_3, formed by the decomposing chelate.

Other propellants varying in the concentration of bonding agent (TEPAN) and solids were prepared using the $Fe(AA)_3$, HAA, ZnO method. Results are shown in Table 56.

b.   R-45M Propellants with Diisocyanates Other Than HDI

Several of the commercially available diisocyanates were screened as alternative curatives for R-45M propellants using the catalyst-suppres-sor scavenger method . These were dianisidine diisocyanate, ditolyl diisocyanate, diphenylmethane diisocyanate, Isonate 143L, isophorone diisocyanate and TDI. Of these, the dianisidine diisocyanate, diphenyl diisocyanate and Isonate 143L were excluded from further study because of insolubility in the binder (dianisidine

TABLE 54

SCREENING OF CHELATING AGENTS IN AN R45M-HDI PROPELLANT
(80 wt% Solids)

Catalyst*	Chelating Agent*	Scavenger*	Rex Hardness After			
			24 hrs	48 hrs	72 hrs	96 hrs
None	None	None	-	nc	nc	10
0.5 Fe(AA)$_3$	5 HAA	None	nc	10	40	50
	5 F$_3$AAH	None	nc	30	50	60
	5 F$_6$AAH	None	24	45	60	60
	5 ϕ_2AAH	None	35	50	55	60
	5 HAA	200 PbO	nc	25	50	55
	5 HAA	200 ZnO	35	50	55	60
	5 HAA	200 ZnS	nc	30	50	60
	5 F$_3$AAH	200 PbO	35	60	60	60
	5 F$_3$AAH	200 ZnO	50	55	60	60
	5 F$_3$AAH	200 ZnS	nc	35	50	55
	5 F$_6$AAH	200 PbO	25	50	55	60
	5 F$_6$AAH	200 ZnO	40	60	60	60
	5 F$_6$AAH	200 ZnS	30	50	60	60
	5 ϕ_2AAH	200 PbO	45	60	60	60
	5 ϕ_2AAH	200 ZnO	50	60	60	60
	5 ϕ_2AAH	200 ZnS	40	60	60	60
	5 HDAc	-	nc	20	30	-
	5 HDAc	200 ZnO	20	35	45	-
↓	5 HDAc	200 PbO	nc	30	45	-

* mg/50g propellant
nc = no cure
HAA = acetylacetone
F$_3$AAH = trifluoroacetylacetone
ϕ_2AAH = diphenylpropanedione
HDAc = dehydracetic acid

TABLE 55

MECHANICAL PROPERTIES OF 85 WT% SOLIDS R-45M-IDP-HDI PROPELLANTS

Catalyst Components, mg/400g					Mechanical Properties at 77°F after 4 days Ambient Temp. Cure*		
$Fe(AA)_3$	$\phi_2 AAH$	$F_6 AAH$	ZnO	PbO	σ_m, psi	ϵ_m, %	E_o, psi
2.5	12.5	--	--	--	123	35	495
2.5	25	--	--	--	129	36	495
2.5	50	--	--	--	118	34	460
2.5	100	--	--	--	111	43	380
2.5	50	--	400	--	119	36	480
2.5	50	--	--	400	127	33	560
2.5	--	25	--	--	94	42	301
5.0	--	50	--	--	79	49	235

* $\dot{\epsilon}$ = 0.74 in/in/min

TABLE 56

EFFECT OF TEPAN and SOLIDS LEVELS ON THE MECHANICAL PROPERTIES
OF R-45M-IDP-HDI PROPELLANTS[a]

% Solids	TEPAN	HDI %	Mechanical Properties After 3 Days Cure at Ambient Temperature		
			σ_m, psi	ϵ_m, %	E_o, psi
85	0.3	0.72	160	35	670
85	0.3	0.69	125	43	450
85	0.3	0.66	81	47	250
88	0.1	0.495	163	24	1030
88	0.1	0.470	106	28	520

(a) Catalyst in all cases was Fe(AA)$_3$ 0.0075%, HAA 0.075%, ZnO 0.1%; $\dot{\epsilon}$ = 0.74 in./in./min; with the R-45 binder system, the tensile strength and elongation vary inversely depending essentially on the quantity of diisocyanate used. For best results the isocyanate level must be optimized.

diisocyanate) or too rapid cure even in the absence of a cure catalyst. The structure of Isonate 143L has not been revealed by the manufacturer (Upjohn Co.).

To establish the optimum levels of catalyst, suppressor and scavenger with the above isocyanate, a number of R-45M prototype propellants were prepared using increasing quantities of $Fe(AA)_3$ only. That concentration of $Fe(AA)_3$ which yielded cured propellants after 1 day at room temperature was tested in propellants containing increasing quantities of HAA (or another chelate) and about 0.1% ZnO, until the desired potlife was obtained. During these tests, it was found that the most critical single parameter affecting the final cure time is the absolute quantity of chelating agent. This is plausible if one considers that catalytic activity is essentially a function of the $Fe(AA)_3$/HAA ratio, and that subsequent inactivation of the HAA is dependent on the absolute quantity of the chelating agent in the propellant. The data indicate that not more than 50 mg of HAA should be used per pound of propellant. At higher levels, too much ZnO is required to neutralize the suppressor. Thus, the lowest $Fe(AA)_3$ concentration which will provide cure should be used. One should bear in mind that the suppressor also acts as stabilizer for the catalyst so that there is less danger of catalyst degradation.

The quantity of catalyst needed for HTPB propellants utilizing TDI, ditolyl diisocyanate and isophorone diisocyanate is significantly higher than for those made with HDI. The properties of propellants prepared with these isocyanates are shown in Table 57 for a number of concentrations of the diisocyanate. These propellants not only require more $Fe(AA)_3$ than those made with HDI to give satisfactory cures, but are also more sensitive to HAA addition, as shown by the considerably higher ratio of $Fe(AA)_3$/HAA. The high concentration of $Fe(AA)_3$ needed (about 10 times higher than for HDI cured batches) also requires a higher, absolute concentration of HAA to obtain the desired potlife. Since the concentration of ZnO cannot be increased indefinitely without sacrificing specific impulse, some slightly longer cure times may have to be accepted.

Aromatic isocyanates are less susceptible to catalysis by ferric compounds than the aliphatic isocyanates. Consequently, the effects on cure are not as drastic when modifications are made on the catalyst system. It appears, for example, that the scavenger (ZnO) contributes only little to the

TABLE 5/

EFFECT OF DIISOCYANATE TYPE ON R-45M-IDP PROPELLANTS CONTAINING 85 WT% SOLIDS

| Diisocyanate | | Catalyst Components, mg/400g | | | Mechanical Properties at 77°F after 4 to 6 days Ambient Temp.Cure* | | |
Type	Level, %	Fe(AA)$_3$	HAA	ZnO	σ_m, psi	ϵ_m, %	E_o, psi
Ditolyl	0.99	25	-	-	169	17	1300
Ditolyl	0.99	25	25	400	154	19	1100
Ditolyl	0.93	12.5	25	-	143	25	780
Ditolyl	0.93	12.5	25	400	147	26	800
Ditolyl	0.875	7.5	15	-	130	28	650
Ditolyl	0.825	7.5	15	-	110	31	510
TDI	0.65	25	-	-	189	19	1100
TDI	0.65	25	25	400	160	25	900
TDI	0.60	12.5	25	-	142	34	620
TDI	0.60	12.5	25	400	149	34	650
TDI	0.58	10	10	-	140	38	535
Isophorone	0.84	25	-	-	170	21	1050
Isophorone	0.80	25	25	400	135	35	540
Isophorone	0.80	12.5	25	-	108	45	370
Isophorone	0.80	12.5	25	400	118	43	420

* $\dot{\epsilon}$ = 0.74 in./in./min

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over-all rate of cure for aromatic isocyanate cured propellants. Of the four diisocyanates tested, TDI provides the best over-all mechanical properties at 77°F.

c. Differences Between Free Radical Initiated (R-45M) and Li Initiated HTPB Prepolymers

Lithium initiated prepolymers usually yield considerably better mechanical properties than the free radical initiated, highly branched R-45M. Furthermore, the high functionality of R-45M (estimated at about 2.5) requires a considerable deficiency of isocyanate groups (NCO/OH ratio about 0.8) if rubbery propellants are to result. The unreacted OH and, therefore, dangling chains do not support external loads but further impair mechanical properties. In the stoichiometrically cured Li HTPB prepolymers there are (at least theoretically) no unreacted chain ends, except those which may be the consequence of poor functionality in prepolymers. The nonstoichiometry in R-45M propellants, as deleterious as it may be for mechanical properties, offers a great advantage for the attainment of a fast and complete cure. To understand this fact consider the following: Besides being more reactive, the hydroxyl groups of the R-45M prepolymer are always in excess, usually not more than 80 equivalent percent of its OH groups are reacted with isocyanate because of R-45M's high functionality. The rate of the urethane reaction is proportional to the concentration of its reactants, or $r = k$ (RNCO) (ROH), which means that towards the end of cure, the rate becomes very small. In the R-45M polymer, RNCO = 0.80 (ROH), i.e. there is always a relatively high concentration of OH groups and the rate is, therefore, accordingly faster, particularly at the final stages of cure. This situation is depicted in Figure 28, where the relative rates of reaction for NCO/OH ratios of 1.0 and 0.8, respectively are plotted. At 98% reaction the nonstoichiometric mixture is about 10 times faster, and at 99% reaction is roughly 20 times faster than the 1:1 mixture.

This explains the great difficulty in obtaining complete cures in Li HTPB propellants, since to achieve optimum and reproducible properties it is important that all hydroxyl functions in the Li prepolymers are reacted with all NCO functions. This becomes clear if we consider the very low crosslink levels required for high strain capability in highly loaded propellants. At a crosslink level of about 0.2×10^{-4} moles chains/cc this necessitates more than 92%

EFFECT OF NONSTOICHIOMETRY ON RATE IN FINAL STAGES OF CURE
IN SECOND-ORDER REACTIONS
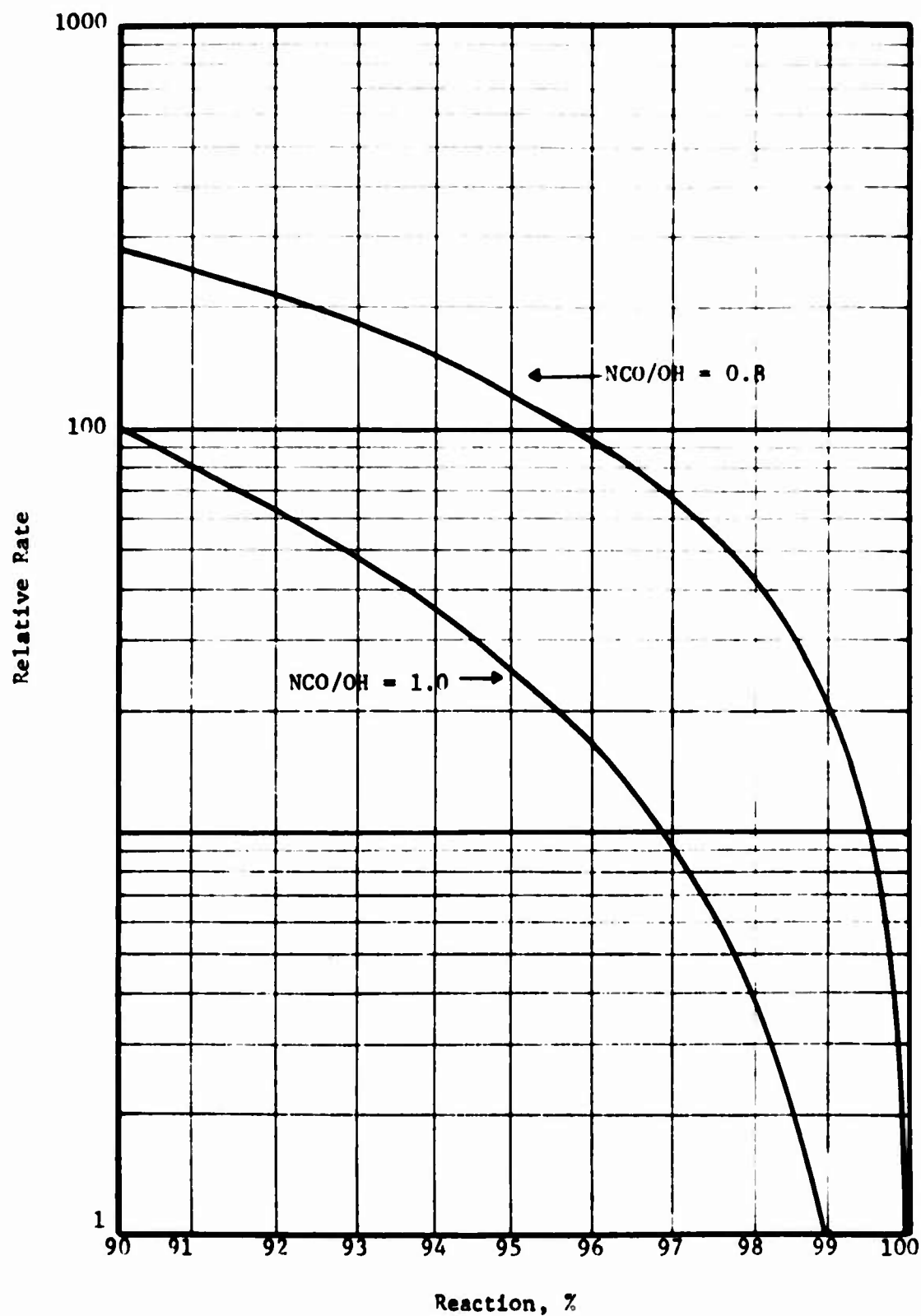
Figure 28

reaction to obtain incipient gelation, and probably better than 98% reaction
to reach full cure, i.e., the desired mechanical properties. In the highly
branched R-45M prepolymer propellants, the latitude is considerably greater.
In addition, interfering impurities play a greater role in the stoichiometrically
cured Li prepolymers, because the ratio of impurity to unreacted hydroxyl groups
becomes very large at the final stages of cure, favoring reaction of the impurity.

The reactivity of the primary hydroxyl groups of Li initiated
HTPB is approximately 1/4 the reactivity of those in R-45M HTPB. This lower
reactivity becomes readily apparent if one attempts to cure propellants using
these prepolymers without catalyst. Some of the cure tests conducted with the
prepolymers, whose relevant properties are listed in Table 58, are shown
in Table 59. The compositions (in grams) of the binders prepared are shown
below. In each case, binders were prepared with and without the AP (80 wt%)
and cured at ambient and at 63°C (145°F).

Lot No.	6/293*	70C	76C	102B	112A	310
HTPB, g	37.37	37.50	39.00	40.20	41.00	40.30
GTRO, g	2.15	5.10	3.28	2.15	1.80	1.44
HDI, g	1.60	4.20	2.72	2.66	2.22	1.85
IDP, g	15.00	15.00	15.00	15.00	15.00	15.00
PBNA, g	0.20	0.20	0.20	0.20	0.20	0.20

* Lot 242AM-293AB/316AM-6

With the exception of the 242AM-293AB/316AM-6 material all prepolymers contain
primary hydroxyl groups. While uncatalyzed propellants using the R-45M-HDI
binder system cure in about 10 days at room temperature or about 3 days at 135°F,
cure of binders based on the Li HTPB, containing secondary OH groups, were
particularly slow. It was not possible to cure uncatalyzed propellants using
this material at any temperature.

The IR absorption in the region 3700-3300 cm^{-1} correlate
well with the reactivity of the alcoholic hydroxyl group. Figure 29 shows the
spectra of some of the prepolymers in the absence of diluents. The sharp band
at 3600 cm^{-1} belongs to the monomeric, unassociated OH group, while the broad

TABLE 58

PROPERTIES OF Li INITIATED PREPOLYMERS

Lot	A831-70C	A831-102B	A831-76C	A831-112A	242AM-310	242AM-293AB/316AM-6
OH, meq/gm	0.954	0.608	0.560	0.500	0.410	0.306
Viscosity at 25°C, poise	32	66	60	123	75	94
MW	1760	2920	2650	3420	4120	4940
H_2O, %	0.025	0.014	0.02	0.018	0.01	0.01
Volatiles, %	0.13	0.16	0.20	0.12	0.4	-
Antioxidant, %	0.28	0.25	0.23	0.20	nil	-
Sulfated Ash, %	<0.01	<0.01	<0.01	<0.01	<0.01	0.07
Functionality						
Non- & mono-functional %	24.3	21.1	29.5	18.6	21.0	-
Difunctional, %	73.4	77.8	68.5	76.1	76.2	75.0
Binder Properties[a]						
Hardness	91	92	93	94	95	93
Plasticity	240	250	245	286	279	271
Gel, %	.	-	82	93	-	89
Unsaturation						
Trans	29.7	34.5	37	36.1	45.6	-
Vinyl	40.6	39.5	36	36.8	25.1	-

[a] Standard binder used to test prepolymer cure properties.

TABLE 59

CURE TESTS WITH L1 INITIATED HTPB PREPOLYMERS

				Days Cure					
1	2	3	4	5	6	7	8	9	10

Binder Cured at Ambient

Lot	1	2	3	4	5	6	7	8	9	10
6/293	ℓ	ℓ	ℓ			ℓ				ℓ
70C	ℓ	ℓ	ℓ			ℓ				ℓ
76C	ℓ	ℓ	ℓ			ℓ				ℓ
102B	ℓ	ℓ	ℓ			ℓ				g
112A	ℓ	ℓ	ℓ			g				sc
310	ℓ	ℓ	ℓ			ℓ				ℓ

Binder Cured at 63°C

Lot	1	2	3	4	5	6	7	8	9	10
6/293	ℓ	sc	sc			0/5				5
70C	g	sc	sc			sc				sc
76C	g	sc	sc			sc				sc
102B	g	sc	sc			5				5
112A	sc	5	5			5				5
310	g	sc	sc			5				5

Binder & AP at Ambient

Lot	1	2	3	4	5	6	7	8	9	10
6/293	nc	nc	nc			nc				nc
70C	nc	nc	nc			nc				nc
76C	nc	nc	nc			nc				nc
102B	nc	nc	nc			nc				nc
112A	nc	nc	nc			nc				15
310	nc	nc	nc			nc				nc

Binder & AP at 63°C

Lot	1	2	3	4	5	6	7	8	9	10
6/293	nc	5/10	10			25				30
70C	nc	40/45	40			50				35/50
76C	nc	30	40/45			60				60
102B	nc	35/40	40			60				50/55
112A	sc	50	55/60			65				60
310	nc	30/40	40			55				50

Legend: ℓ = liquid, g = gelled (does not flow), sc = soft cure, nc = no cure (corresponds to gelled above). Numbers are Rex hardness readings.

INFRARED SPECTRA OF SOME PREPOLYMERS

Figure 29
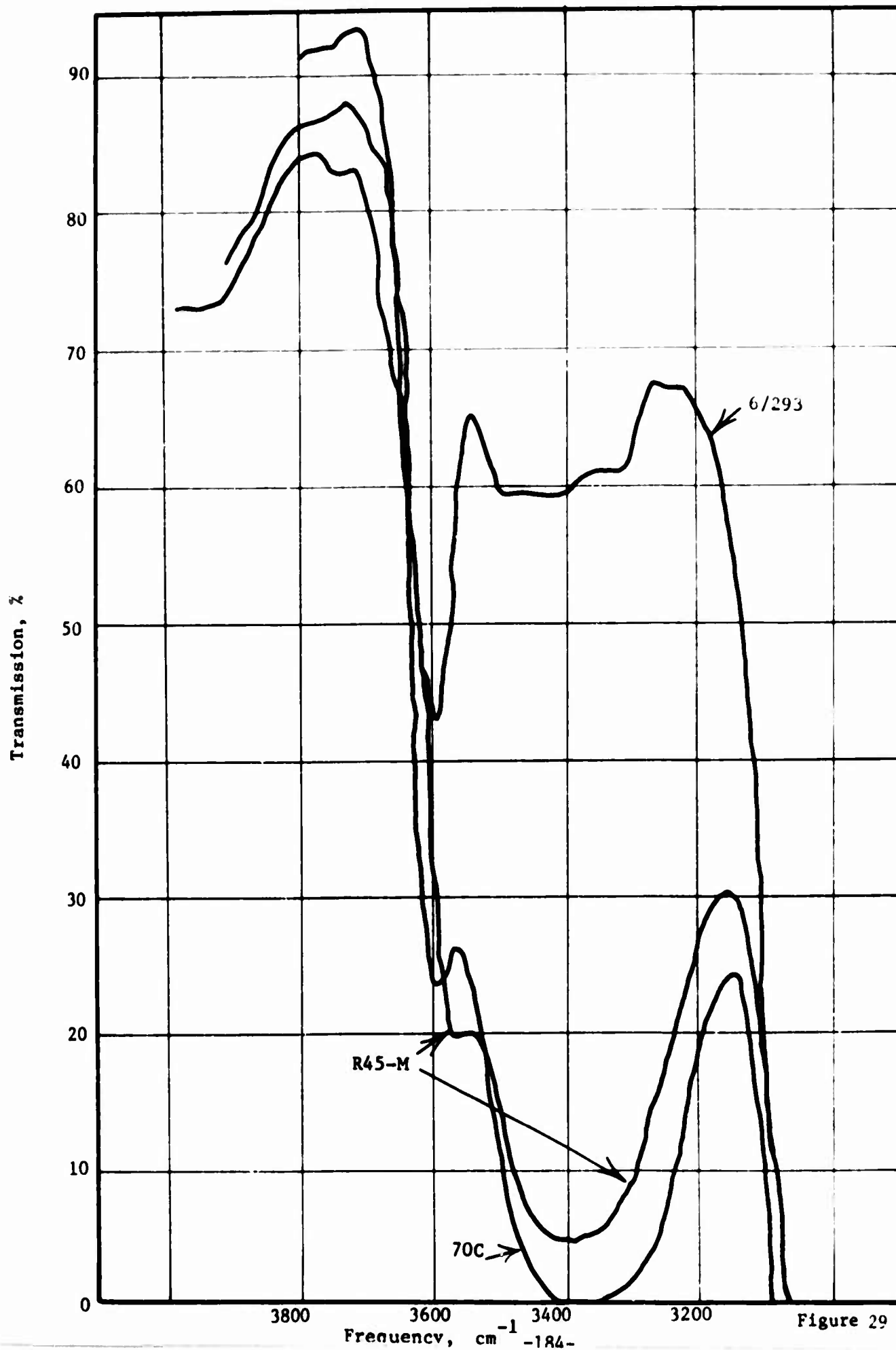
band (maximum about 3370 cm^{-1}) is due to the associated, hydrogen-bonded polymer OH groups. As discussed at the beginning of this report those alcoholic species which react the fastest show the largest degree of association of the hydroxyl group.

Figure 29 shows that in the very slow reacting, secondary, OH terminated 242AM-293AB/316AM-6 prepolymer (which is practically uncurable in the absence of catalyst) the monomeric form predominates, while in the faster reacting, primary hydroxyl containing prepolymer (Lot 70C), the associated alcohol by far outweighs the unassociated species. The fastest reacting HTPB (R-45M) shows the monomeric form only as an inflection (shoulder) in the associated band. The greater adsorbance of Lot 70C at 3360 cm^{-1} is due to the lower equivalent weight of this prepolymer. In Table 60 the absorbance ratios of monomeric to associated bands are listed for some of the investigated prepolymers. If the prepolymers are diluted such that the OH concentration is constant, the spectra become very similar (Figure 30). Those of the primary OH terminated prepolymers are represented by 242AM-310 resembling that of the 1-octanol, and the secondary OH group carrying prepolymer 242AM-293AB/316AM-6 resembles that of 2-octanol. Diluent was 1,7-octadiene in order to keep the chemical nature of the different specimens as close as possible.

The different degree of association which is seen to be a function of concentration as well as the nature of the OH group is of importance only in uncatalyzed or weakly catalyzed propellants, where the uncatalyzed reaction contributes significantly to the over-all cure, or where the catalyst decomposes during cure and the final cure proceeds essentially via the uncatalyzed reaction.

The better mechanical properties achieved with Li HTPB propellants are due primarily to the lesser amount of dangling chains. As far as cure is concerned, the low functionality of a prepolymer can, of course, be offset by a higher concentration of crosslinker, but mechanical properties are impaired as a result of the larger proportion of ineffective network. Table 61 shows the effect of crosslinker concentration on mechanical properties of propellants based on the secondary hydroxyl terminated 316AM-6/242AM-293 prepolymer. The

TABLE 60

RELATIVE IR ABSORBANCES[a] FOR OH MONOMER AND POLYMERS FOR VARIOUS HTPB PREPOLYMERS

Lot No.	A_{3400}/A_{3600}
2-Octanol[b]	0.73
1-Octanol[c]	1.25
242AM-293AB/316AM-6	0.56
242AM-310	1.29
A831-112A	1.50
A831-76C	1.74
A831-102B	2.00
R-45	2.00[d]
A831-70C	4.43

[a]Monomer, 3600 cm^{-1}; polymer, 3350 to 3400 cm^{-1} (greatest absorbance in this region). Generally a smear with 0.4mm thickness.

[b]Mixed with 1,7-octadiene to simulate eq. wt. 3200.

[c]Mixed with 1,7-octadiene to simulate eq. wt. 3000.

[d]Band at 3600 cm^{-1} discernible only as a shoulder on polymer band.

IR ABSORPTION SPECTRA OF PREPOLYMERS AND 1- AND 2-OCTANOL DILUTED WITH 1,7-OCTADIENE TO CORRESPOND TO AN EQUIVALENT WEIGHT OF 3250 – WIDTH .4mm, 25°C

Figure 30
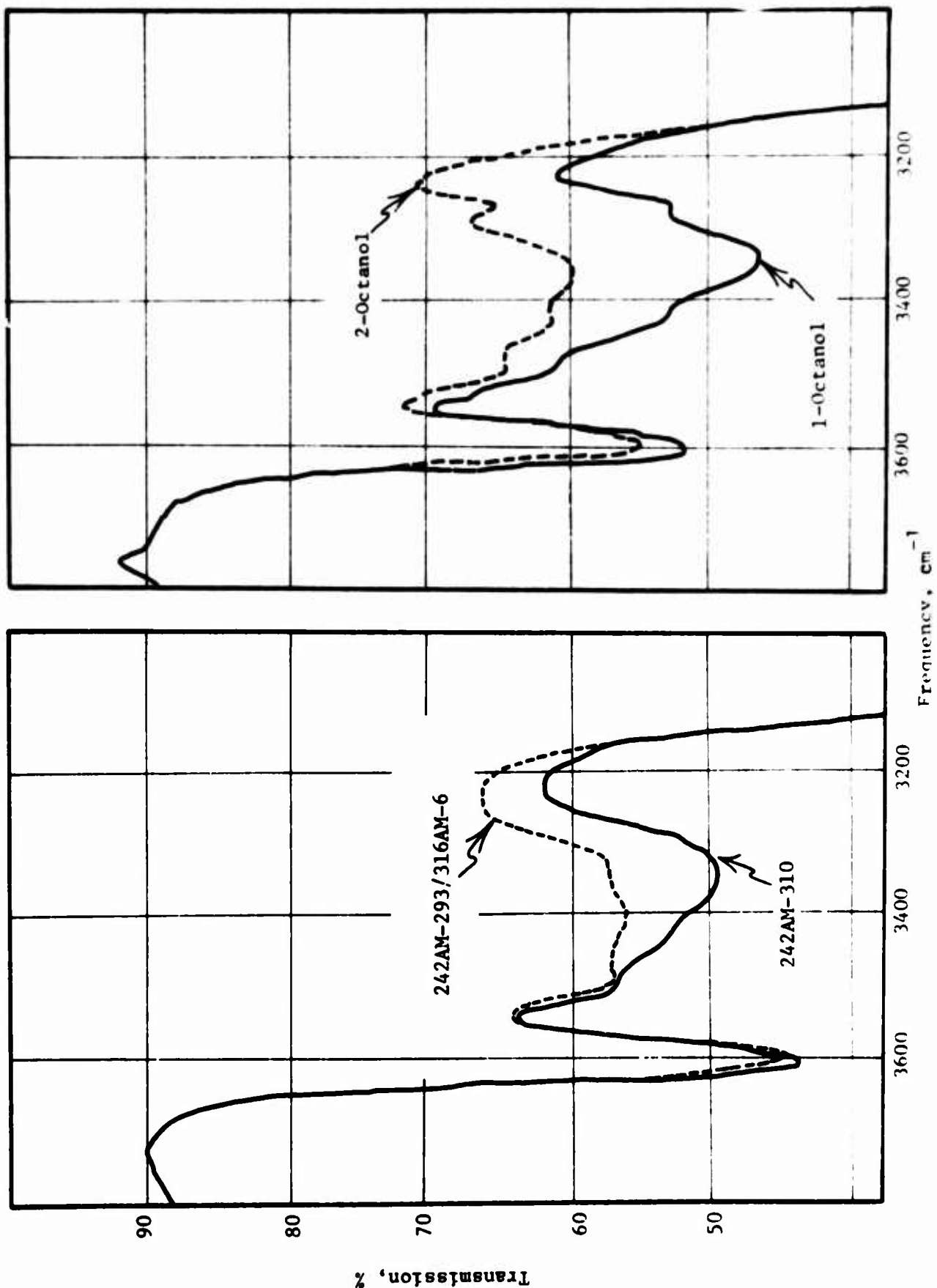
TABLE 61

EFFECT OF CROSSLINK LEVEL ON THE UNIAXIAL TENSILE PROPERTIES OF 85 WT% SOLIDS HTPB[a] PROPELLANT AT 77°F[b]

GTRO, Equivalents	Rex Hardness after 4 days (r.t.)	After Cure 6 days r.t.			After Aging 14 Days 160°F		
		σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi
20	30	34	120	150	36	120	145
25	45	55	97	180	51	90	180
30	50	72	85	215	88	93	200
35	65	104	58	310	127	65	325
40	70	122	47	380	161	53	410

[a] Lot 316AM-6/242AM-293 cured with HDI; catalyst Fe(AA)$_3$ 0.0025%.
[b] Standard JANAF Tensile Specimens, $\dot{\epsilon}$ = 0.74 min^{-1}.

catalyst concentration used (0.0025% $Fe(AA)_3$) resulted in a potlife of about 30 minutes, which was insufficient to yield void-free castings. At this rather high level of catalysis, very little (if any) postcure is observed after aging.

d. Li Initiated HTPB Prepolymers

(1) $Fe(AA)_3$ - Diketone-ZnO System

Since the first four of the prepolymers shown in Table 58 were in short supply (only 1 gal of each was available), most of the work was done with the polymer Lots 242AM-310 (primary functional groups) and 24.. -93/316AM-6 (secondary OH groups) of which larger quantities were available. These two lots also yield better mechanical properties. The properties obtained with 85 wt% solids propellant as a function of the crosslinker concentration are shown in Table 61.

Without catalyst, propellants using either prepolymer[*] did not cure even after 14 days at 135°F. By contrast, propellants prepared with R-45M cure in the absence of catalyst in one week at ambient temperature (or about 2 days at 135°F). This may indicate that the frequency of NCO consuming side reactions is much greater in these prepolymers than in R-45M. Polyether propellants fail to cure if the cure is delayed too long, e.g., by insufficient catalysis, presumably because of their high water content.

Several chelating agents have been tested as suppressers. The more reactive ones like hexafluoroacetylacetone and trifluoro-acetylacetone do not need the ZnO scavenger, since they are eliminated through reaction with the Al powder. In fact, the hexafluoroacetylacetone is so unstable in the presence of aluminum that it is unsatisfactory. In addition, there is evidence that the iron tris(trifluoroacetylacetonate) and particularly the iron tris(hexafluoroacetylacetonate) undergo spontaneous decomposition to the inactive and insoluble FeF_3.

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[*] Propellants differ from the cure tests reported in Table 59 by lower cross-link density, binder fractions, presence of bonding agents and aluminum, all factors which will adversely affect cure stoichiometry. With higher NCO concentrations than is present in the catalyzed propellants, cure may be affected in some cases.

The data of Table 62 show that the prepolymers
from the General Tire and Rubber Company are much more susceptible to changes
in catalysis than the free radical initiated R-45M polymer. Thus, extending
the potlife results in a softer cure[*], and the longer the potlife, the softer
the cure. For example, a propellant, which shows no signs of cure during the
first three days after preparation (in the absence of catalyst) can no longer
be cured if catalyst is added or the temperature is raised or both. Cures of such
propellant batches can only be effected if some additional isocyanate is added.
This is evidence for NCO consuming side reactions in the uncatalyzed propellant
and the extent of these side reactions is greater in Li HTPB formulations[**] than
R-45M formulations. Thus, if the same state of cure is to be obtained for long
potlife propellants, slight adjustments in the NCO level have to be made, i.e.,
a long potlife requires a slightly higher concentration of NCO than a propellant
where the initial cure reaction is faster. The extent to which this adjustment
is possible[*] is shown in Tables 67 and 68.

Further evidence that side reactions are consuming
part of the curing agent is shown in the 160°F aging data, which were obtained
for some of the propellants. If just slow (and hence incomplete) cure were
responsible for the lower tensile properties obtained during ambient temperature
curing, the subsequent 160°F aging should result in considerable postcure[*].
However, the data in Table 62 show that this is not the case, since stable prop-
erties are obtained during the ambient cure.

Table 63 shows the mechanical properties of 85 wt%
solids propellants obtained with the other GT&R polymers. A comparatively high
concentration of $Fe(AA)_3$ (0.005%) was used to ensure positive cure. Accordingly,
these propellants had only a very short potlife (about 30 minutes at ambient)
and the mechanical properties were tested after 2 days of ambient cure. Apparently,
full cure was not obtained in this short time since considerable postcure took
place during 4 days at 180°F. A comparison of these mechanical properties with those
listed in Table 61 shows that better mechanical behavior is achieved with pre-
polymer Lot 242AM-293/316AM-6.

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* This discussion does not consider the probable effect of duration of cure
on chain length distribution (see Section C.3) since methods to assess
this have not been worked out.

** Lot 242AM-293/316AM-6 (secondary OH groups) was considerably more difficult
to cure than Lot 242AM-310 (primary OH groups).

TABLE 62

EFFECT OF CATALYST MODIFICATIONS ON POTLIFE AND MECHANICAL PROPERTIES OF 85 WT%
SOLIDS L1 HTPB-HDI PROPELLANTS

| Catalyst System | | | Rex Hardness After 24 hrs | Uniaxial Tensile Properties @ 77°F[a] | | | | | |
| | | | | After 7 Days Ambient Cure | | | After 14 days Aging at 160°F | | |
$Fe(AA)_3$, %	Suppressor, %	Scavenger, %		σ_m psi	ϵ_m %	E_o psi	σ_m psi	ϵ_m %	E_o psi
0.0025	—	—	50	104	58	310	127	65	325
0.0013	—	—	40	97	63	295	108	60	300
0.0025	HAA, 0.0013	ZnO, 0.1	<20(c)	113	70	290	-	-	-
0.0025(b)	HAA, 0.0013	ZnO, 0.1	<20(c)	123	61	435	-	-	-
0.0025(b)	HAA, 0.000	ZnO, 0.1	flows	112	73	411	-	-	-
0.0013	HAA, 0.0007	ZnO, 0.1	20	101	75	285	99	72	264
0.0013	HAA, 0.0013	ZnO, 0.1	<20(c)	83	71	230	74	74	231
0.0013	HAA, 0.0025	ZnO, 0.1	flows	63	100	187	61	93	180
0.0013	HF_6AA, 0.0013	—	35	101	68	308	105	63	288
0.0013	HF_6AA, 0.0025	—	30	104	78	295	103	68	286
0.0013	$H\emptyset_2AA$, 0.0025	—	<20(c)	97	75	277	-	-	-
0.0013	$H\emptyset_2AA$, 0.0025	—	<20(c)	94	64	281	-	-	-
0.0013	$H\emptyset_2AA$, 0.005	—	<20(c)	33	26	90	-	-	-
0.0013	$H\emptyset_2AA$, 0.0025	ZnO, 0.1	<20(c)	111	67	352	-	-	-
0.002	HF_3AA, 0.0013	—	45	107	67	341	-	-	-
0.002	HF_3AA, 0.0025	—	<20(c)	92	83	264	-	-	-
0.002	HF_3AA, 0.0050	—	flows	53	92	154	-	-	-
$Fe(\emptyset_2AA)_3$									
0.0025	HF_3AA, 0.0025	—	flows	61	86	147	-	-	-
0.0025	HF_3AA, 0.005	—	flows	23	102	66	-	-	-
$Fe(F_3AA)_3$									
0.0025	HF_3AA, 0.0013	—	flows	94	76	257	-	-	-
0.0025	HF_3AA, 0.0025	—	flows	75	63	231	-	-	-
0.0025	HF_3AA, 0.0050	—	flows	24	77	77	-	-	-

(a) Standard JANAF Tensile Specimens, $\dot{\epsilon} = 0.74$ min^{-1}.
(b) After second day both propellants were cured for 2 days at 70°C.
(c) Propellants too soft to measure.

TABLE 63

MECHANICAL PROPERTIES OF 85 WT% SOLIDS PROPELLANTS

		Uniaxial Tensile Properties at +77°F[a]							
		After 2 days Ambient Cure			After 4 days aging at 180°F				
Prepolymer	Equivalent GTRO	σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi		
A 831-70C	30	110	33	446	129	32	530		
A 831-76C	20	78	69	156	89	77	189		
A 831-102B	20	140	47	545	138	51	387		
A 831-112A	20	112	57	286	166	42	820		

[a]Standard JANNAF Tensile Specimens, $\dot{\epsilon} = 0.74$ min^{-1}.

The solids loading of propellants utilizing prepolymer 242AM-310 were increased to 88 wt%. In these propellants trimodal oxidizer blend containing 35/30/35 parts of $405\mu/80\mu/7\mu$ average particle size oxidizer was used. All propellants contained 35 equivalents of CTRO as crosslinker. Results of propellant batches made are presented in Table 64. Comparison of results for 7 and 24 day room temperature cure shows that 7 days are not sufficient to reach full cure with the catalyst/suppressor system used.

(2) Cure Compensation Studies with Excess HDI

The data of Tables 65 and 66 indicate that postcure in the Li initiated prepolymers is insignificant provided full cure has been reached prior to aging. However, as explained previously, the attainment of full cure with Li HTPB prepolymers is more difficult than with the R-45M prepolymers where the higher reactivity and excess OH groups ensure full cure. In addition, the level of impurities in Li initiated prepolymers appears larger, which tends to consume more NCO groups. Some evidence for this premise is shown in Table 67. Propellant 1 containing 0.0025% of ferric tris-(1,3-diphenyl-1,3-propanedionate), $Fe(\phi_2AA)_3$, without suppressor cured completely in 7 days at room temperature. Unfortunately, the potlife of such a propellant is very short, less than one hour at ambient temperature. In the second propellant, cure has been slowed by addition of 0.0025% HF_3AA, and the potlife is about 4 hours. This allows NCO consuming side reactions to participate to a larger extent resulting in softer cure[*], which is even more pronounced in Propellant 3, where 0.005% HF_3AA gave the propellant more than adequate potlife. However, full cure was not obtained in Propellant 3 as evidenced from the rise in σ_m and E_o during aging. Propellants 2A and 2B both contain 10% excess HDI. Since ambient cure was very slow, one of these propellants was put into 180°F cure. The additional HDI obviously prevented the loss of modulus and tensile properties which occurred in Propellant 2. Finally, Propellants 4 and 5 which contained no catalyst were not cured in more than 15 days, regardless of cure temperature (up to 180°F). In a separate test using significantly higher HDI concentrations, one propellant

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[*] Again nonrandom chain length distribution may contribute to the effect in the slower curing propellant.

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TABLE 64

PROPERTIES OF L1 HTPB PROPELLANTS CONTAINING 88 WT% SOLIDS

(HTPB Lot 242AM-310, Propellants Cured 7 and 24 Days at Ambient Temperature)

| Catalyst System | | Scavenger | Rex Hardness after 24 Hrs. | Uniaxial Tensile Properties at 77°F[a] | | |
Catalyst	Suppressor			σ_m psi	ϵ_m %	E_o psi
Fe(AA)$_3$, 0.002 % ;	HF$_3$AA 0.0025 %	--	30	88 (126	40 34	350 572)[b]
Fe(AA)$_3$, 0.002 % ;	HAA 0.002 %	--	20	90 (127	41 33	330 540)[b]
Fe(AA)$_3$, 0.002 % ;	HAA 0.002 %	Z_nO, 0.1%	20	95 (125	41 34	370 556)[b]
Fe(F$_3$AA)$_3$ 0.0025 % ;	HF$_3$AA 0.0013 %	--	45	113 (131	34 34	517 580)[b]
Fe(Ø$_2$AA)$_3$ 0.0025 % ;	HF$_3$AA 0.0013 %	--	30	94 (126	41 33	352 563)[b]

[a] Standard JANNAF Tensile Specimens, $\dot{\epsilon}$ = 0.74 min^{-1}.

[b] 24 days cure.

TABLE 65

EFFECT OF AGING ON THE MECHANICAL PROPERTIES OF 88 WT% SOLIDS
PROPELLANTS MADE WITH Li INITIATED HTPB

(Propellants Aged 2 Weeks at +160°F)

	Uniaxial Tensile Properties at 77°F[a]		
	σ_m, psi	ϵ_m, %	E_o, psi
Ambient Cure 8 Days			
Propellant 1[b]	117	36	405
Propellant 2[c]	119	39	572
Propellant 3[d]	90	37	396
Ambient Cure 16 Days			
Propellant 1	112	35	402
Propellant 2	116	36	563
Propellant 3	99	36	410
Propellants Cured 8 Days at Ambient After 2 Weeks Aging at 160°F			
Propellant 1	124	41	410
Propellant 2	119	38	590
Propellant 3	97	37	370

(a) Standard JANAF Tensile Specimens, $\dot{\epsilon}$ = 0.74 in./in./min.

(b) Catalyst 0.0025% $Fe(AA)_3$

(c) Catalyst 0.0012% $Fe(AA)_3$

(d) Catalyst 0.0025% $Fe(AA)_3$/0.0012% HAA

TABLE 66

AGING OF 88 WT% SOLIDS L1 HTPB PROPELLANTS PREPARED WITH PREPOLYMER
LOT 242AM-293/316AM-6

Cure Conditions		Uniaxial Tensile Properties					
Temperature	Time	Initial Properties			Properties after Aging Two Weeks at 160°F (at +77°F[a])		
		σ_m, psi	ε_m, %	E_o, psi	σ_m, psi	ε_m, %	E_o, psi
Ambient	4 days	72	43	300	145	34	640
	4 days	102	34	450	135	35	560
135°F	4 days	135	32	640	141	34	610
	4 days	140	33	620	145	34	650

[a]Standard JANNAF Tensile Specimens, $\dot{\varepsilon}$ = 0.74 in./in./min.

TABLE 67

EFFECT OF STATE OF CURE ON AGING OF 88 WT% SOLIDS PROPELLANTS

BASED ON L1 INITIATED HTPB

(Secondary OH Groups)

| | | Uniaxial Tensile Properties at 77°F[a] | | | | | |
| | | 8 days ambient cure | | | 16 days aging at 160°F | | |
Propellant	Catalyst	σ_m,psi	ε_m,%	E_o,psi	σ_m,psi	ε_m,%	E_o,psi
1	Fe(ϕ_2AA)$_3$ 0.0025%	150	48	500	147	43	519
2	Fe(ϕ_2AA)$_3$ 0.0025%, + HF$_3$AA 0.0025%	102	55	370	108	57	385
3	Fe(ϕ_2AA)$_3$ 0.0025%, + HF$_3$AA 0.005%	33	57	99	76	53	260
2A[b]	Fe(ϕ_2AA)$_3$ 0.0025%, + HF$_3$AA 0.0025%	169	43	800	174	33	875
2B[c]	Fe(ϕ_2AA)$_3$ 0.0025%, + HF$_3$AA 0.005%	too soft to measure			161	33	800
4	Uncatalyzed	uncured			uncured		
5[c]	Uncatalyzed	uncured			uncured		

[a] Standard JANNAF Tensile Specimens, $\dot{\varepsilon}$ = 0.74 in./in./min.

[b] Propellant was cured 3 days at ambient, then 4 days at 180°F, it also had 10 equivalents % excess HDI.

[c] 10 Equivalents % excess HDI.

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having 20% excess HDI, showed soft cure after 2 weeks at 180°F. The slow cure
of these prepolymers is surprising, since even uncatalyzed PPG propellants cure
in about three days at 180°F.

The effect of excess HDI was studied further with
the propellants shown in Table 68. Propellants 1-4 contain 0.002% $Fe(\phi_2AA_3)$
and 0.002% ϕ_2AAH; suppressant was necessary for sufficient potlife to obtain
flaw free castings. After about 1 day at ambient temperature, all propellants
were cured three days at 180°F. The data indicate a distinct possibility of
crosslinking through allophanate linkages at these higher temperatures. To
check this possibility further, Propellants 5 and 6 were prepared without suppress-
ant. After 1 day at room temperature (Rex hardnesses were 50 and 65, respectively)
one half of each propellant was allowed to continue cure at ambient, the other
half was cured at 180°F for an additional three days. While the properties of the
100 equivalents % HDI containing propellant remain unchanged, the properties of
Propellant 6 changed lending support to the premise that allophnate linkages
are being formed at the higher temperature.

e.   Use of Acids as Catalyst Suppressor

The $Fe(AA)_3$/HAA/ZnO method also works in the Li initiated
propellants, but further improvement is needed if full cure (combined with
adequate potlife) is to be accomplished in less than 2 weeks. The restoration
of the catalytic activity of the $Fe(AA)_3$ depends largely on the removal of the
free HAA from the system. The rate of consumption is strongly dependent on the
concentration of the scavenger ZnO and the acidity of the diketone. Other
diketones like diphenylpropanedione, triacetylmethane and benzoylacetylacetone
have been tried but have not shown significant improvement over HAA. Trifluoro-
and hexafluoroacetylacetone were the only two diketones which are consumed signi-
ficantly faster than HAA, particularly the hexafluoro compound. However, cure
difficulties were encountered, which are apparently caused by the subsequent
decomposition of the ferric hexafluoroacetylacetonate into inactive FeF_3; the
trifluoro compound is somewhat more stable. Since the approach to finding a
more reactive (but otherwise stable) diketone was not too successful, a new
approach was investigated. It consisted of using acids as suppressors for the
$Fe(AA)_3$ catalyst, which according to

TABLE 68

EFFECT OF HDI CONCENTRATION OF PROPERTIES OF 85 WT% SOLIDS
HTPB PROPELLANTS BASED ON L1 INITIATED PREPOLYMERS

(Secondary OH Groups, 3 Day Cure at 180°F)

Propellant	HDI Equivalent %		Uniaxial Tensile Properties at +77°F [a]		
			σ_m, psi	ϵ_m, %	E_o, psi
1	100		64	108	180
2	104		118	78	480
3	107		150	70	580
4	110		190	43	850
5[b]	100	cure at ambient	55	80	110
5a	100	cure at 180°F	55	70	110
6[b]	110	cure at ambient	123	32	560
6a	110	cure at 180°F	160	45	730

[a] Standard JANNAF Tensile Specimens, $\dot{\epsilon}$ = 0.74 in./in./min.
[b] Propellants 5 and 6 contain a different oxidizer blend than Propellants 1-4. Propellants 5 & 6 contain no suppressant. After curing one day at room temperature, half of each propellant was placed at 180°F.

$$\mathrm{Fe(AA)}_3 + \mathrm{HX} \rightleftharpoons \mathrm{Fe(AA)}_2\mathrm{X} + \mathrm{HAA}$$

also yields free HAA with a concommitant effect on catalyst activity. It is much easier to find acids than diketones with the proper degree of reactivity, i.e., compounds which will be consumed neither too fast nor too slow in order to yield the desired balance of cure and potlife.

Table 69 shows the effect of acids on the relative rate of the methanol-HDI reaction as determined by the exotherm method. Clearly, the stronger acids produce the larger effect, since the equilibrium is shifted more to the right. That the species $\mathrm{Fe(AA)}_2\mathrm{X}$ is actually formed can be concluded from two observations: (1) a color change from red to dark brown-red upon addition of the acid, and (2) an activity minimum at the composition mixture corresponding to $\mathrm{Fe(AA)}_2\mathrm{Cl}$ (Table 44), while $\mathrm{Fe(AA)}_2\mathrm{OOCC}_7\mathrm{H}_{15}$ shows a maximum. The latter appears to be much less stable than $\mathrm{Fe(AA)}_2\mathrm{Cl}$, and on treatment with hexane, the ferric octoate can be extracted leaving the $\mathrm{Fe(AA)}_3$ behind. Some of these compounds are valuable catalysts and were prepared and tested (see Section D.7).

The effects of suppressors on the catalytic activity of T-12 (i.e., dibutyltin dilaurate) were also tested. The results are listed in Table 70.

All acids which have a pKa of 6 or lower will yield a satisfactory potlife. The acids tested include acetic, chloroacetic, α-chloro-octanoic, α-bromotetradecanoic, linoleic, mandelic (phenylhydroxyacetic), benzilic (diphenylhydroxyacetic), lactic, pyruvic, phenylacetic, p-nitrophenylacetic and p-toluenesulfonic acid. Of these, the best appear to be the α-hydroxyacids, mandelic and benzilic acids.

The advantage of acid over diketone is greater reactivity with the scavenger thus faster restoration of catalyst activity and a resultant shortening of overall time of cure. A disadvantage is that acid is also more reactive with the isocyanate than diketone which might be objectionable in some cases. This reaction with NCO is minimized in the stronger acids which yield a more stable intermediate, e.g., RNCO + HCl ⟶ RNHCOCl; RNHCOCl + ROH ⟶ RNHCOOR + HCl yielding urethanes. Weaker carboxylic acids first form a mixed

TABLE 69

EFFECT OF ACIDS ON THE RATE OF THE $Fe(AA)_3$ CATALYZED

METHANOL-HDI REACTION AT 25°C

(Concentration $Fe(AA)_3$ = 2.6 x 10^{-3}M)

Acid	Concentration $M \times 10^3$	Relative Rate
None	-	1
Acetylacetone	10	0.12
Perchloric	4	0.19
"	10	0.08
Nitric	4	0.15
"	10	0.10
Hydrocloric	4	0.16
"	10	0.10
p-Toluenesulfonic	4	0.21
"	10	0.10
Benzilic	4	0.12
"	10	0.07
Citric	10	0.09
α-Chloroacetic	10	0.22
Acetic	10	0.65
Linoleic	10	0.58
α-Chlorooctanoic	10	0.30
α-Bromotetradecanoic	10	0.25

TABLE 70

EFFECT OF ACIDS AND HAA ON THE RATE OF DIBUTYLTIN DILAURATE CATALYZED
1-BUTANOL-HDI REACTION AT 25°C

(Catalyst Concentration = 4.2×10^{-3}M)

Additive	Concentration M x 10^3	Relative Rate
None	-	1.0
Linoleic Acid	20	0.65
p-Toluenesulfonic Acid	10	0.10
Acetylacetone	200	0.07

anhydride (carbamic acid-carboxylic acid anhydride) which decomposes to the corresponding amide, e.g., $RNHCOOCOR \longrightarrow RNHCOR + CO_2$. Although less favored than the urethane reaction, this reaction can and does occur yielding some undesirable chain termination. Therefore, where faster cure times are desired, a good compromise appears to be a combination of HAA and acid, to lessen chain termination without sacrificing too much of the faster rate of cure. To illustrate this point, consider a typical formulation using the Li initiated prepolymer. The composition of the binder is about 22×10^{-3} equivalents isocyanate and hydroxyl groups and 4×10^{-3} equivalents crosslinker in a pound of propellant. The quantity of acid required to produce an adequate effect on potlife is around one millimole. On a percentage basis, this is a small proportion of the propellant, but with respect to the crosslinking level this quantity of acid can be significant, if it enters into the reaction.

The catalyst-acid approach has also been successfully applied to the dibutyltin dilaurate (T-12) catalyst, for which up to now no suppressor was available. T-12 was included into these studies in order to develop a catalyst system for propellants where surface hardening may be a major problem.

(1) Application of the Acid Suppressor Method to Li HTPB Propellants

The results obtained with propellants utilizing the slow curing, secondary OH terminated, Li HTPB are shown in Table 71. Obviously, full cure was not achieved in 7 days cure at room temperature, even though ZnO was added to speed the process. It was found that Zn catalysts like $Zn(AA)_2$ or fatty acid salts show little catalytic effect with this type of prepolymer. The use of other metal oxides or salts such as $Fe(OH)CO_3$, $PbCO_3$, $ZnCO_3$, Fe_2S_3, PbO, or metals such as Mg, Fe, Zn were also relatively ineffective with this prepolymer. Numerous tests have shown that ZnO and PbO are probably the most useful scavengers.

In the faster curing, primary OH terminated, Li initiated prepolymers, it is advantageous to retain some HAA so that the required acid concentration is not too high. Table 72 shows the results obtained with propellants prepared with the primary terminated 242AM-310, and 831AM-112B

TABLE 71

ACID USED AS CATALYST SUPPRESSOR IN SLOW CURING SECONDARY OH TERMINATED HTPB PROPELLANT

(85 Wt % Solids)

	Uniaxial Tensile Properties at 77°F[a]					
	Cure 7 days r.t.			7 days r.t. + 48 hrs 180°F		
Catalyst System	σ_m psi	ϵ_m %	E_o psi	σ_m psi	ϵ_m %	E_o psi
Fe(AA)$_3$ 0.25% HAA 0.0013%	103	80	242	113	74	295
Fe(AA)$_3$ 0.25% linoleic acid 0.01%, ZnO 0.1%	96	84	191	114	75	270
Fe(AA)$_3$ 0.25% linoleic acid 0.02%, ZnO 0.1%	87	99	160	117	89	240
Fe(AA)$_3$ 0.25% α-bromotetradecanoic acid 0.01%, ZnO 0.1%	107	70	270	121	69	303

[a]Standard JANNAF Tensile Specimens, $\dot{\epsilon}$ = 0.74 min^{-1}.

TABLE 72

EFFECTS OF ACIDS AND HAA AS CATALYST SUPPRESSORS IN 85 WT% SOLIDS PROPELLANTS

(Primary Terminated HTPB Lots 242AM-310 and 831AM-112A)

| Number | Suppressor-Scavenger[a] | Prepolymer Lot | Uniaxial Tensile Properties at 77°F[b] | | | | | |
| | | | Cure at Ambient | | | Cure at Ambient + 4 Days at 180°F | | |
			σ_m, psi	ε_m, %	E_o, psi	σ_m, psi	ε_m, %	E_o, psi
1	Chloroacetic Acid 0.4[c]	242AM-310	137	53	613	154	60	630
2	Chloroacetic Acid 0.4, ZnO 0.1%	242AM-310	148	45	655	165	50	660
3	Benzilic Acid 0.2	242AM-310	93	99	350	84	76	405
4	Benzilic Acid 0.2, ZnO 0.1%	242AM-310	137	67	560	165	67	640
5	Linoleic Acid 0.5, ZnO 0.1%[d]	242AM-310	105	69	383	139	76	473
6	Linoleic Acid 0.5, ZnO 0.1%[c]	831AM-112A	100	48	255	-	-	-
7	Linoleic Acid 0.5, PbO 0.1%[c]	831AM-112A	128	42	374	-	-	-
8	Acetylacetone 0.1, -	831AM-112A	117	33	410	-	-	-
9	HAA 0.1, Linoleic 0.5, ZnO 0.1%[c]	242AM-310	92	86	365	-	-	-
10	HAA 0.1, Linoleic 0.5, -	242AM-310	71	97	286	-	-	-
11	HAA 0.1, Benzilic 0.25, ZnO 0.1%	242AM-310	90	89	310	-	-	-
12	HAA 0.1, Chloroacetic 0.5, ZnO 0.1%	242AM-310	120	63	479	-	-	-
13	HAA 0.2, ZnO 0.1%	242AM-310	72	97	281	-	-	-

[a] All contain 0.0025% Fe(AA)$_3$, suppressor concentration is given in mmoles/lb propellant

[b] Standard JANNAF Tensile Specimens, $\dot{\varepsilon} = 0.74$ min^{-1}.

[c] 6 Days ambient cure

[d] 4 Days ambient cure

prepolymer lots. For propellants prepared with the latter prepolymer, no crosslinker was used, indicating that this polymer has an effective functionality of greater than 2. As can be seen from Table 72 various stages of cure have been obtained by changing the suppressor-scavenger system and the cure promoting effect of ZnO is readily apparent (cf., Propellants 1 and 2, 3 and 4, 9 and 10).

The use of the acid alone in the concentrations shown in Table 72 does not provide sufficient propellant potlife (between 2 and 3 hrs were obtained), however, a satisfactory potlife is obtained with the combination. Although Propellants 9 and 13 have about the same potlife, cure proceeded considerably faster in the propellant containing HAA and acid combination than that with HAA alone as a result of the more rapid disappearance of the acid.

The rate retarding effect is greater with the stronger acid. For example, benzilic acid suppresses the catalytic activity more strongly than linoleic acid. An exception are the α-halogen substituted acids, which show poor suppressant action in propellants. However, these compounds are very effective quarternizing reagents and may therefore be rapidly consumed by the amine type bonding agent present in these propellants. There is also evidence that the elongation is adversely affected by these acids and, therefore, they were dropped from further consideration. Viscosity buildup data for four propellants using only the acid as suppressor are shown in Table 73. Obviously, the potlife achieved with the acid alone is not good enough, but the potlife is improved to satisfactory levels in the combination HAA-acid, as shown in Table 74.

The acid suppressor method works also with the T-12 (dibutyltin dilaurate) catalyst, as shown for Propellant 3 in Table 74. About the best mix viscosities are obtained if diethanolamine is used as bonding agent (Propellant 2 in Table 74). However, in the case shown, as well as for T-12, the cure stoichiometry was apparently not optimum, and propellant mechanical properties are poor.

The propellants shown in Table 75 were made to assess a potential effect of TEPAN on cure and properties. The data indicate a slight retardation on cure. More significant (besides bonding) is a definite effect of TEPAN on propellant modulus. Thus, it

TABLE 73

EFFECT OF ACIDS ON THE POTLIFE OF 85 WT% SOLID PROPELLANTS

(Primary Terminated HTPB Lot 242AM-310)

Infinite Shear Viscosity (poise) at 77°F

No. 1		No. 2		No. 3		No. 4	
Hours	Poises	Hours	Poises	Hours	Poises	Hours	Poises
1	58,300	1.3	11,000	1.7	244,000	2	67,000
3	445,000	3.2	53,000	3.8	824,000	4	153,000
		5.2	130,000			6	470,000
		7.2	360,000				

Mechanical Properties[b] at 77°F after 20 Days Cure at Ambient Temp.

No.	Catalyst System	σ_m, psi	ϵ_m, %	E_o, psi
1	Fe(AA)$_3$ 0.0025%, ZnO 0.1%, chloro-acetic acid 0.5[a]	159	44	730
2	Fe(AA)$_3$ 0.0025%, ZnO 0.1%, benzilic acid 0.25	156	86	630
3	Fe(AA)$_3$ 0.0025%, ZnO 0.1%, linoleic acid 0.5	138	76	470
4	Fe(AA)$_3$ 0.0025%, ZnO 0.1%, HAA 0.1	108	75	545

[a]Acid concentrations in mmoles/400g propellant
[b]Standard JANNAF tensile specimens, $\dot{\epsilon} = 0.74$ min^{-1}

TABLE 74

POTLIFE AND PROPERTIES OF 85 WT% PROPELLANTS USING THE HAA-ACID SUPPRESSOR COMBINATION

(Primary Terminated HTPB Lot 242AM-310)

Infinite Shear Viscosity at 77°F

No. 1		No. 2		No. 3	
Hours	Poise	Hours	Poise	Hours	Poise
1	10,000	1.3	7,000	1.2	9,000
3	23,000	3.2	12,000	3.2	17,000
5	60,000	5.2	21,000	5.2	33,000
7	138,000	7.2	42,000	7.2	62,000
9	263,000	9.2	74,000	9.2	98,000
		11.2	168,000	11.2	148,000
		13.5	259,000		

Properties at 77°F[a]
(14 Days Ambient Cure)

No.	Catalyst System	σ_m, psi	ϵ_m, %	E_o, psi
1	0.0025% FeAA, .05 HAA[b], 0.025 benzilic acid, 0.1% ZnO	137	76	630
2	0.0025% FeAA, .05 HAA[b], 0.025 benzilic acid, 0.1% ZnO[c]	38	75	209
3	0.0025% T-12, 0.025% para-toluene sulfonic acid	52	94	280

[a] Standard JANNAF tensile specimens, $\dot{\epsilon} = 0.74$ min^{-1}

[b] Concentration of HAA and acid in mmoles/400g propellant

[c] Propellant contained diethanolamine 0.025% instead of TEPAN

TABLE 75

EFFECT OF TEPAN ON CURE AND MECHANICAL PROPERTIES OF L1 HTPB PROPELLANTS

85 Wt% Solids, Lot 242AM-310

No.	Propellant[a] Solids	Tepan, %	Rex Hardness				Uniaxial Properties at 77°F[b] After 20 Days Ambient Cure		
			1 day	2 days	3 days	6 days	σ_m, psi	ϵ_m, %	E_o, psi
1	Only oxidizer[c]	–	15	30	40	45	19	65	140
2	Oxidizer with aluminum	–	15	30	40	50	25	50	210
3	Only oxidizer[c]	0.1	<10	15	30	60	123	105	365
4	Oxidizer and aluminum	0.1	<10	15	40	60	139	75	490
5	Oxidizer and aluminum	0.025	15	25	35	55	49	62	312
6	Oxidizer and aluminum	0.05	<10	15	35	60	80	70	402
7	Oxidizer and aluminum	0.075	<10	15	40	60	110	65	450

[a]Catalyst system: 0.0025% (Fe(AA))$_3$, 0.05 mmoles HAA, 0.25 mmoles benzilic acid, 0.1% ZnO

[b]Standard JANNAF tensile specimens; $\dot{\epsilon}$ = 0.74 min^{-1}.

[c]The solids loading in propellants not containing Al was 82.5% b.w.

appears that part of the compound acts as crosslinker, which is not really surprising if one considers its solubility in the binder phase and its high functionality. This fact must be considered if TEPAN is to be used in other propellant systems.

Table 76 shows the results obtained with modifications of the T-12 catalyst system. T-12 is very sensitive to acid addition as well as the presence of scavengers like ZnO. For example, a 85 wt% propellant cured satisfactorily with 0.25 mmoles PTS and 0.1% ZnO but cured poorly in the absence of the ZnO. When the acid concentration was doubled the propellant failed to cure. The lower selectivity of tin catalyst, may also cause catalysis of the acid-NCO reaction, which would explain this high sensitivity of the T-12 cure system to impurities in general.

The effect of other acids on mechanical properties are listed in Tables 77 and 78 for the pure acid and the acid-HAA suppressor combination. The data obtained, when processing variations were attempted, show that it is prudent to withhold $Fe(AA)_3$ until the final stages of batch preparation.

Data shown in Table 79 give mechanical properties over the temperature range from +160°F to -40°F of 10-lb propellant batches made with some catalyst systems. As expected, the catalyst system per se has no effect on temperature dependence of mechanical properties. If the propellant cures harder, we obtain stiffer properties over the entire temperature range and vice versa.

(2) Ferric Catalysts of the $Fe(AA)_2X$ Type

Section D.7 contained a list of ferric compounds, which were derived from $Fe(AA)_3$ by substituting one acetylacetonate ligand with an acid radical to yield compounds of the type $Fe(AA)_2X$. Four of these, namely ferric bis(acetylacetonato)chloride, $Fe(AA)_2Cl$, ferric bis(acetylacetonato)perchlorate, $Fe(AA)_2ClO_4$, ferric bis(acetylacetonato)mandelate, $Fe(AA)_2OOCCHOHC_6H_5$, and ferric bis(acetylactonato)p-toluenesulfonate were tested in propellants, the mechanical properties of which are shown in Table 80. In these propellants, 0.2 millimoles HAA/400g propellant were used as suppressor. Dibutyltin dilaurate

TABLE 76

MODIFICATION OF DIBUTYLTIN DILAURATE CATALYZED BY ACIDS

85 Wt% Solids, Lot 242AM-310[b]

Catalyst System	Rex Hardness			Mechanical Properties at 77°F[a] 14 Days Ambient Cure		
	1 day	2 days	5 days	σ_m, psi	ϵ_m, %	E_o, psi
0.0025% T-12	70	70	70	157	40	750
0.0025% T-12, 0.25 PTS, 0.1% ZnO	10	35	55	107	73	437
0.0025% T-12, 0.25 linoleic acid, 0.1% ZnO	10	35	55	100	94	363

[a] Standard JANNAF tensile specimens, $\dot{\epsilon}$ = 0.74 min^{-1}

[b] Curative is HDI

TABLE 77

TEST OF ACID SUPPRESSORS IN 85 WT% SOLID PROPELLANTS

(242AM310 HTPB Prepolymer)

Catalyst 0.0025% Fe(AA)$_3$, 0.1% ZnO, 0.25 mmoles Acid Suppressor	Uniaxial Tensile Properties 77°F[a] 12 Days – Ambient Cure		
	σ_m, psi	ϵ_m, %	E_o, psi
Phenylacetic acid	150	49	631
pNitrophenylacetic acid	135	39	682
Mandelic acid	93	38	488
Lactic acid	119	62	506

[a]Standard JANNAF tensile specimen, $\dot{\epsilon} = 0.74$ min^{-1}

TABLE 78

85 WT% PROPELLANTS CONTAINING NITROPHENYLACETIC AND MANDELIC ACID AS SUPPRESSORS FOR Fe(AA)$_3$

(242AM310 Prepolymer Lot)

Suppressor[b] (mmoles)		Uniaxial Tensile Properties at 77°F[a] Ambient Cure					
		7 days			20 days		
		σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi
Mandelic acid	0.25	90	101	358	123	66	596
Mandelic acid	0.25[c]	35	91	165	83	72	430
Mandelic acid	0.25[d]	93	97	333	127	71	605
p-Nitrophenylacetic acid	0.25	136	48	444	145	52	622
p-Nitrophenylacetic acid	0.5	114	67	165	119	70	517

[a] Standard JANNAF tensile specimen, $\dot{\epsilon} = 0.74$ min^{-1}

[b] All contain 0.0025% Fe(AA)$_3$, 0.05 mmoles HAA and 0.1% ZnO

[c] Fe(AA)$_3$, HAA and mandelic acid were added to premix prior to mixing, while ordinarily all components of the catalyst system with the exception of the ZnO are added at the end of the mixing cycle together with the diisocyanate.

[d] HAA and acid were added as in (c) but Fe(AA)$_3$ was withheld until HDI addition.

TABLE 79

MECHANICAL PROPERTIES OF HTPB PROPELLANTS (242AM310 PREPOLYMER)
CONTAINING 88 AND 85 WT% SOLIDS CURED WITH HDI AFTER 30 DAYS AMBIENT CURE

| | Solids % | Uniaxial Tensile Properties[a] at | | | | | | | | | | |
| | | +160°F | | | 77°F | | | 0°F | | | -40°F | | |
		σ_m psi	ε_m %	E_o psi	σ_m psi	ε_m %	E_o psi	σ_m psi	ε_m %	E_o psi	σ_m psi	ε_m %	E_o psi
Propellant 1[b]	88	79	35	391	132	48	609	187	56	1360	279	58	2300
Propellant 2[c]	85	62	51	273	115	65	540	170	77	890	284	56	2000
Propellant 3[d]	85	85	39	455	138	51	620	185	61	1240	281	41	2360

[a] Standard JANNAF Tensile Specimens, $\dot{\varepsilon} = 0.74$ min^{-1}

[b] Catalyst system: 0.0025% Fe(AA)$_3$, 0.1 mmoles HAA, 0.1% ZnO

[c] Catalyst system: 0.0025% T-12 (dibutyltin dilaurate), 2.5 mmoles PTS, 0.1% ZnO

[d] Catalyst system: 0.0025% Fe(AA)$_3$, 1 mmole HAA, 2.5 mmoles benzilic acid and 0.1% ZnO

TABLE 80

NEW IRON CATALYSTS TESTED IN 85 WT% PROPELLANTS

(Primary HTPB Lot 242AM310/HDI)

Catalyst[b]		Uniaxial Tensile Properties at $77°F$[a] - Cure at Ambient										
		6 days			14 days			20 days			30 days		
		σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi
$Fe(AA)_2Cl$	0.0025%	86	81	295	140	47	613	165	45	721	177	45	840
$Fe(AA)_2ClO_4$	0.0025%	20	66	149	102	80	390	140	73	541	156	71	570
$Fe(AA)_2OCOCHOHC_6H_5$	0.0025%	31	80	198	123	75	480	151	58	622	162	40	720
$Fe(AA)_2$ PTS	0.0025%	-	-	-	97	84	390	118	80	440	133	85	420
Dibutyltin dilaurate[c]		27	92	169	101	94	363	135	75	488	158	75	600

[a] Standard JANNAF tensile specimens, $\dot{\epsilon} = 0.74$ min^{-1}

[b] Catalyst system includes 0.2 millimoles HAA/400g propellant, and 0.1% ZnO

[c] 0.0025%; 0.25 mmoles linoleic acid, 0.1% ZnO

is included for comparison. All of these propellants with the exception of
the one containing $Fe(AA)_2Cl$ catalyst had adequate (>8 hrs) potlife. Since
cure proceeded slowly, the amount of HAA was cut back to C.15 millimoles HAA.
With the exception of the $Fe(AA)_2Cl$ catalyst, potlife was still satisfactory.
The data for the latter propellants are presented in Table 81. As shown in
Tables 80 and 81 these catalysts yield propellants with mechanical properties
equivalent to other ferric catalysts. In addition, they are water soluble,
in contrast to $Fe(AA)_3$, and may therefore be useful for some special appli-
cations where water solubility is desirable. In PBD propellants there is no
particular advantage over the more readily available $Fe(AA)_3$.

(3) Scale-Up to 88 Wt% Solids

The 242AM-310/IDP/HDI or TDI propellant has been
scaled up to 88 wt% solids. Table 82 shows the tensile properties of three
large (10-lb) batches in which the concentration of the crosslinker was varied
to obtain optimum properties. Catalyst system was 0.0025% $Fe(AA)_3$ and 0.1 mmoles
HAA. As shown in Table 82, cure is not complete after 1 week at ambient
temperature. The propellant with 15 equivalents crosslinker (glycerol triri-
cinoleate) was chosen for further testing in large batches with the more promising
catalyst systems. The composition of the binder matrix was as follows: Lot 310
68.5%; GTRO 1.8%; stabilizer 1.4%; IDP 25%, TDI 3.1% or an equivalent quantity
of HDI. In addition, the propellants contain 0.1% TEPAN bonding agent with its
incremental share of the curative.

The properties of the unfilled binders (binder does
not contain TEPAN) are given below.

Curing Agent	σ_m, psi	ε_m, %	E_o, psi	v_2	M	Stress Decay (2 min.)
TDI	>32	>500	18	0.076	45000	33%
HDI	>34	>500	18	0.076	45000	27%

The v_2 value was determined from swelling in benzene.
From Figure 23 and with a μ factor of 0.4, the effective molecular weight between
crosslinks is found to be 45000. This figure agrees well with the substantial
stress decay measured on these binders. The measured crosslink density would be

TABLE 81

NEW IRON CATALYSTS TESTED IN 85 WT% PROPELLANTS

(HTPB Lot 242AM310 Cured with HDI)

Uniaxial Tensile Properties[a] at 77°F
Cure at Ambient

Catalyst[b]		7 days			12 days			28 days		
		σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi
$Fe(AA)_2Cl$	0.0025%	123	58	457	140	42	591	155	39	785
$Fe(AA)_2ClO_4$	0.0025%	60	86	171	106	76	594	128	66	576
$Fe(AA)_2OCOCHOHC_6H_5$	0.0025%	88	98	299	142	59	594	165	47	791
$Fe(AA)_2O_3SC_6H_4CH_3$	0.0025%	-	-	-	86	86	319	140	66	600

[a]Standard JANNAF tensile specimen; $\dot{\epsilon} = 0.74$ min^{-1}
[b]Catalyst system includes 0.15 mmoles HAA and 0.1% ZnO

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TABLE 82

PROPERTIES OF 88 WT% SOLID PROPELLANTS PREPOLYMER LOT 242AM-310
CURED WITH HDI

Crosslinker, Equivalents	Uniaxial Tensile Properties at 77°F[a]								
	7 Days Ambient Cure			7 Days Ambient + 1 day 180°F					
	σ_m,psi	ϵ_m,%	E_o,psi	σ_m,psi	ϵ_m,%	E_o,psi			
20	120	54	440	163	41	730			
15	69	59	380	102	60	480			
10	31	50	190	94	65	460			

[a]Standard JANNAF tensile specimens; $\dot{\epsilon}$ = 0.74 min^{-1}

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$0.75 \times 1/45000 = 1.7 \times 10^{-5}$ moles chains/cm^3, since only 75% of the total binder is network. This, of course, does not consider other ineffective structure, like zero functional prepolymer chains, etc.

If we assume the 242AM-310 to be difunctional (which it probably is, despite claims to being only 75% difunctional) and the GTRO to be trifunctional, the average molecular weight of chains between crosslinks can be calculated from the composition using eq. 10 and is found to be 27000. This figure appears to be in reasonable agreement with the swelling value, considering the uncertainties of the functionality values.

When these two binders are loaded to 88% solids with AP and Al the properties at 77°F and a strain rate of 0.74 min^{-1} are those tabulated below. A high level of catalysis and cure at 135°F were used to ensure positive cure.

Curing Agent	σ_m, psi	ϵ_m, %	E_o, psi
HDI	154	22	1200
TDI	128	31	800

Thus incorporation of the filler raises the modulus of the binder by a factor of approximately 70.

The best catalyst-suppressor-scavenger system has been applied to these propellants. The properties are listed in Tables 83 and 84. There are, of course, variations of cure involved which probably affected the cure stoichiometry as well as the distribution of chain lengths. Comparison of the mechanical property data of Tables 83 and 84 shows again that TDI produces better propellants than HDI. This has to be bought at the expense of a slightly more sluggish cure. In Propellants 1 and 2 of Table 84 the glycerol triricinoleate crosslinker is replaced by the same number of equivalents of a tri-isocyanate, PAPI* and CTI respectively. PAPI-3 seemed not to be soluble in the binder premix (cloudiness results upon addition of PAPI to a HTPB binder premix)

* Purified and extracted PAPI was used, as described by A. J. DiMilo. AFRPL-TR-71-56, Final Technical Report, Contract F04611-70-C-0016, May 1971.

TABLE 83

ACID SUPPRESSORS USED WITH TDI IN PRIMARY HTPB
PROPELLANTS (LOT 242AM-310); 88 WEIGHT % SOLIDS

No.	Suppressor[a], mmoles/400g	Uniaxial Tensile Properties at 77°F[b]											
		10 day Amb. Cure			30 day Amb. Cure			14 day 160°F Aging				
		σ_m psi	ϵ_m %	E_o psi	σ_m psi	ϵ_m %	E_o psi	σ_m psi	ϵ_m %	E_o psi		
1	None	50	51	210	208	40	880	235	47	970		
2	0.33 benzilic acid	69	56	380	162	55	630	161	54	550		
3	0.33 p-toluene-sulfonic acid	99	54	410	199	51	780	180	53	650		
4	0.33 pyruvic acid	56	51	280	189	48	750	191	47	800		

[a]Catalyst system contained in addition: 0.008% $Fe(AA)_3$, 0.004% HAA and 0.1% ZnO.

[b]Standard JANNAF tensile specimens; $\dot{\epsilon} = 0.74$ min^{-1}.

TABLE 84

PROPERTIES OF 10-LB PROPELLANT BATCHES (88% SOLIDS) USING VARIOUS
MODIFICATIONS AND THE PRIMARY HTPB LOT 242AM-310

No.	Curative	Suppressor[b] mmoles/400g	Uniaxial Tensile Properties at 77°F[a]								
			14 day ambient			30 day ambient			14 day 160°F		
			σ_m psi	ϵ_m %	E_o psi	σ_m psi	ϵ_m %	E_o psi	σ_m psi	ϵ_m %	E_o psi
1	PAPI/HDI/TDI	Benzilic Acid 0.33	70	58	290	96	50	340	103	65	314
2	CTI/TDI	Benzilic Acid 0.33	132	52	440	164	43	600	180	49	620
3	HDI	Mandelic Acid[c] 0.25	124	49	540	149	45	690	157	52	680
4	HDI	p-Nitrophenyl-acetic Acid[d] 0.25	139	43	700	147	46	800	169	51	640

[a] Standard JANNAF tensile specimens; $\dot{\epsilon}$ = 0.74 min^{-1}.

[b] Catalyst system: 0.008% Fe(AA)$_3$, 0.004% HAA and 0.1% ZnO.

[c] Catalyst system: 0.004% Fe(AA)$_3$, 0.004% HAA and 0.1% ZnO.

[d] Catalyst system: 0.004% dibutyltin dilaurate, 0.1% ZnO.

which might be responsible for the relatively soft cure obtained with that combination. For convenience the PAPI was dissolved in HDI at an equivalence ratio of 1 PAPI/2 HDI.

Comparison of the propellant mechanical properties with other similar data shows that they are equal to the best formulations reported.

The mixed HAA/acid suppressor method is, of course, also applicable to R-45M propellants for which Table 85 gives some examples. The considerably poorer properties of these propellants are a consequence of the more highly branched prepolymer. The rather sophisticated mixed HAA/acid method is really not necessary for the R-45M. It appears that ZnO and acid yields about as good properties. Moreover, ZnO or PbO will not catalyze autoxidation, and are therefore more satisfactory where surface hardening may be a problem.

F. CURE STABILITY AND AGING OF AMBIENT TEMPERATURE CURED HTPB PROPELLANTS

Table 86 shows the aging stability of a polyether-polyurethane propellant of the type in the Minuteman Wing I missiles. Practically none of these propellants showed postcure and during high temperature aging, they underwent a good deal of softening. Some of these propellants showed exceptional stability, as the C-1 propellant depicted in Table 87.

In contrast, HTPB propellants usually exhibit postcure, and on aging may either increase or decrease in hardness, the former being more frequently encountered.

It is readily seen that postcure would be much more of a problem in HTPB matrices than in polyether binders. The latter contain much larger quantities of water, which during the final stages of cure, consume residual NCO groups. Another characteristic of polyether propellants (at least those with PPG which absorbs moisture strongly) is their comparatively short cure time. This, of course, has the same cause as the absence of postcure. In fact PPG propellant will either cure in 4 days, or if not, will not

TABLE 85

MECHANICAL PROPERTIES OF 88 WT% SOLID PROPELLANTS
USING THE R-45M PREPOLYMER AND HDI OR TDI CURES

Propellant[b]	Curative[c]	Uniaxial Tensile Properties[a] at 77°F		
		σ_m, psi	ε_m, %	E_o, psi
1	HDI	121	26	715
2	HDI	125	29	660
3	HDI	142	28	790
4	TDI	144	27	800
5	TDI	151	24	910

(a) Standard JANNAF tensile specimens, $\dot{\varepsilon} = 0.74$ min^{-1}

(b) Catalyst system:

   (1) 0.1% ZnO

   (2) 0.0007% Fe(AA)$_3$, 0.125 mmoles HAA, 0.25 mmoles mandelic acid and 0.1% ZnO

   (3) 0.0007% Fe(AA)$_3$, 0.125 mmoles HAA, 0.5 mmoles linoleic acid and 0.1% ZnO

   (4) 0.5 mmoles linoleic acid and 0.1% ZnO

   (5) 0.5 mmoles linoleic acid and 0.1% PbO

(c) Cured 7 days at room temperature

TABLE 86

STORAGE STABILITY OF POLYETHER TYPE PROPELLANT

(Minuteman Wing I Propellant - ANP-2862 JM Mod 1)

Weeks Stored at 180°F	Uniaxial Tensile Properties[a] at 77°F		
	σ_m, psi	ϵ_m, %	E_o, psi
Initial Properties[b]	120	33	751
2	102	33	712
6	106	40	600
10	102	36	638
14	105	36	638
18	98	28	662
22	98	31	669

[a] Standard JANNAF Tensile Specimen, $\dot{\epsilon} = 0.74$ min^{-1}

[b] After 7 days cure at 110°F

TABLE 87

MECHANICAL PROPERTIES OF POLYETHER-POLYURETHANE PROPELLANT[a] AFTER ACCELERATED AGING

Uniaxial Instron Data: Strain Rate 0.74 min.$^{-1}$

Test Temp., °F		Unaged	8 Days 220°F	14 Days 220°F	1 Month 180°F	4 Months 180°F	3 Months 150°F
150	σ_m, psi	107	94	112	106	121	112
	ϵ_m, %	21	23	40	28	33	29
	E_o, psi	872	883	636	817	809	873
77	σ_m, psi	173	184	180	205	207	205
	ϵ_m, %	45	48	54	52	53	42
	F_o, psi	1020	867	697	875	997	1120
-40	σ_m, psi	432	373	314	389	354	434
	ϵ_m, %	69	73	73	73	66	73
	E_o, psi	2650	3510	3010	3250	3850	2650

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[a]Composition (wt %): NH_4ClO_4 67; aluminum 17; CuO202, a burning rate accelerator 0.1; sulfur, stabilizer 0.1; N-phenylnaphthylamine, stabilizer 0.1; Fe(AA)$_3$ 0.015; HAA 0.009; polyether-polyurethane binder containing 25% isodecyl pelargonate 15.68%.

cure regardless of the temperature to which it may be subjected.

In HTPB binders the level of impurities (H_2O) appears to be much less so that residual NCO groups continue reacting, slowly increasing the hardness of the propellants. Even with the best catalyst systems developed on this program slight postcure was observed after ambient cures of 30 days duration. This is the case for the stoichiometrically cured Li HTPB. R-45M propellants, because of the excess of OH groups in the matrix, do not show significant postcure. However, they seem particularly apt to harden during aging, the reason for which is not clear. Table 88 shows data which indicate that hardening occurs even after 6 months at room temperature. After this time, it would be safe to assume that no unreacted isocyanate groups remain. One of the propellants listed in Table 88 did not contain the ferric catalyst. Thus, one may conclude that, at least at the level tested, the ferric ion does not significantly contribute to this hardening. In Table 89 more aging data of these two propellants are shown, which further corroborate the above conclusions. Table 90 lists aging data on uncatalyzed R-45M propellants which again exhibit this gradual hardening, regardless of whether they were cured at ambient temperature or 135°F. Propellant 1 in Table 90 used the R-45M prepolymer as received, while in Propellant 2 the R-45M prepolymer was mixed with antioxidants and subjected to 180°F for 24 hours, prior to use in the propellant. This treatment was designed to destroy traces of peroxide which might be left in the commercial product and which could cause additional crosslinking through vinyl polymerization. Again, a steady hardening of the propellants is observed which persists during aging even after 20 days cure at 135°F. It is interesting to note that the ambient cured propellants achieved higher modulus and tensile strength. (Ambient and 135°F cures were conducted on the same propellant master batch.) The origin of this effect is not clear, but persists also in catalyzed versions of the above propellants. Table 91 shows a similar aging profile for the catalyzed propellants. Propellant 1 was catalyzed with $Fe(AA)_3$ only, while Propellant 2 also contained the suppressor HAA. In Propellant 1, cure should be essentially completed after 2-3 days at ambient, while Propellant 2 should have taken somewhat longer. Again there is an increase in modulus and tensile strength after aging at 160°F while the room temperature properties remain essentially unchanged. Table 92

TABLE 88

EFFECT OF AGING ON MECHANICAL PROPERTIES OF R-45M PROPELLANTS

85 wt% Solids

Aging Condition, Temp. °F for 6 months	Propellant	Uniaxial Tensile Properties at 77°F[a]		
		σ_m, psi	ϵ_m, %	E_o, psi
Room Temperature	1[b]	108	44	390
110	1	117	42	356
160	1	167	32	682
Room Temp. + 4 weeks at 160	1	134	42	480
Room Temperature	2[c]	104	43	390
110	2	128	42	405
160	2	159	27	721
Room Temp. + 4 weeks at 160	2	140	35	503

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[a]Standard JANNAF Tensile Specimen, $\dot{\epsilon}$ = 0.74 min.

[b]TDI, catalyst ZnO/HAA 0.1%/0.025%.

[c]HDI, catalyst $Fe(AA)_3$/HAA/ZnO; 0.001%/0.01%/0.1%.

TABLE 89

AGING OF 85 WT% SOLIDS R-45M HTPB PROPELLANTS

Propellant[a]	Cure Time at room Temp, days	Initial Properties σ_m psi	ϵ_m %	E_o psi	Time Days	110°F σ_m psi	ϵ_m %	E_o psi	135°F σ_m psi	ϵ_m %	E_o psi	160°F σ_m psi	ϵ_m %	E_o psi
1	10	83	54	215	25	-	-	-	-	-	-	133	44	390
1	35	101	50	275	3	97	50	265	98	50	264	104	49	280
					7	102	54	275	102	54	275	112	41	330
					17	-	-	-	112	43	300	-	-	-
2	10	78	42	220	25	-	-	-	-	-	-	135	40	430
2	35	86	44	250	3	97	45	260	95	43	268	102	48	280
					7	96	45	260	102	46	295	116	46	320
					17	-	-	-	118	42	340	-	-	-

a Propellant 1: TDI, Catalyst ZnO/HAA, 0.1%/0.025%;
Propellant 2: HDI, Catalyst FeAA/HAA/ZnO, 0.001%/0.01%/0.1%

TABLE 90

AGING OF UNCATALYZED 85 WT% SOLIDS R-45M PROPELLANTS

Propellant[b]	Cure Time Days Ambient	Cure Time Days 135°F	Uniaxial Tensile Properties at 77°F [a] Initial Properties σ_m, psi	ϵ_m, %	E_o, psi	Properties after 2 Weeks Aging at 160°F σ_m, psi	ϵ_m, %	E_o, psi
1	4	-	-	uncured	-	-	-	-
	-	4	89	37	255	113	41	380
	10	-	106	37	400	150	35	610
	-	10	109	39	380	125	34	430
	20	-	117	35	430	163	32	650
	-	20	133	40	450	144	31	490
2	4	-	-	uncured	-	-	-	-
	-	4	105	34	330	118	36	400
	10	-	125	33	510	149	36	620
	-	10	115	36	420	128	35	520
	20	-	128	31	540	158	35	670
	-	20	135	37	480	151	29	540

a   Standard JANAF Tensile Specimens, $\dot{\epsilon}$ = 0.74 in./in./min.

b   Propellant 1: Uncatalyzed 85 wt% solid R-45M/IDP/HDI propellant; Propellant 2: Same as 1, but prepolymer was heat treated with antioxidants prior to use in order to destroy traces of peroxide.

TABLE 91

AGING OF CATALYZED R-45M-HDI PROPELLANTS AFTER VARIOUS CURE CONDITIONS

Propellant	Cure Time, Days		Uniaxial Tensile Properties at +77°F[a]					
	Ambient	135°F	Initial Properties			Properties after 2 Weeks Aging at 160°F		
			σ_m, psi	ϵ_m, %	E_o, psi	σ_m, psi	ϵ_m, %	E_o, psi
1[b]	4	-	142	33	560	150	27	600
	-	4	137	35	500	160	35	610
	10	-	133	34	530	156	34	650
	-	10	143	32	520	173	29	630
	20	-	135	35	550	163	31	640
	-	20	143	30	550	178	28	670
2[c]	4	-	122	40	475	148	29	550
	-	4	123	46	410	143	41	450
	10	-	123	37	460	151	34	580
	-	10	130	40	430	157	31	520
	20	-	123	35	470	164	30	600
	-	20	141	37	460	171	29	610

(a) Standard JANAF Tensile Specimens, $\dot{\epsilon}$ = 0.74 in./in./min.

(b) Fe(AA)$_3$ = 0.001%

(c) Fe(AA)$_3$ = 0.001%, HAA - 0.01%

TABLE 92

LONG TERM AGING DATA ON R-45M/IDP/HDI PROPELLANTS
(85% Solids)

Propellant	Aging Condition		Uniaxial Tensile Properties at 77°F[a]		
	Time, mos.	Temp°F	σ_m, psi	ϵ_m, %	E_o, psi
No. 1, Table 90	4	room	125	36	490
No. 2, Table 90	4	room	140	33	630
No. 1, Table 91	4	room	141	35	600
No. 2, Table 91	4	room	135	38	520
No. 1, Table 90	4 + 2	room + 160	155	34	620
No. 2, Table 90	4 + 2	room + 160	147	29	600
No. 1, Table 91	4 + 2	room + 160	177	27	720
No. 2, Table 91	4 + 2	room + 160	169	32	650
No. 1, Table 90	5	160	186	31	840
No. 2, Table 90	5	160	175	29	800
No. 1, Table 91	5	160	195	29	950
No. 2, Table 91	5	160	191	30	900

[a]Standard JANNAF Tensile Specimen; $\dot{\epsilon} = 0.74$ min^{-1}.

shows some long term 160°F aging data on these propellants. Table 93 shows that the bonding agent TEPAN is not the cause for this effect because propellants without it show the same hardening. These data make it probable that the hardening of R-45M propellants during high temperature aging is most probably a secondary chemical reaction, which is independent of the urethane cure reaction. Other aging data on R-45M propellants are listed in Tables 43, 49 and 50.

Propellants using the Li initiated HTPB shows the same hardening effect during high temperature aging, but to a lesser degree. Unlike the R-45M propellants, Li HTPB propellants are apt to show some postcure, particularly in the weakly catalyzed versions. The only long term aging data obtained on a secondary hTPB, Lot 242AM-293/316AM-6, are shown in Table 94 for two 88 wt% solids propellants, varying slightly in catalyst system. Other aging data on Li HTPB propellants are contained in Tables 61, 62, 65, 66, 67, 72, 83 and 84.

In conclusion, aging of propellants is more often than not affected by certain components, rather than the binder backbone. For example the C-1 propellants were found to age better than those with triethanolamine as the bonding agent (cf Tables 86 and 87). MT-4 batches were found to gradually soften on aging. Often the cure catalyst accelerates degradative reactions during aging. For example, tin compounds are known for this. Thus reliable evidence as to the aging characteristics of the binder system proper can be only obtained on uncatalyzed propellants. However, the latter are practically unobtainable with the Li HTPB.

G. ANALYSIS OF PROPELLANT MATRICES BY SWELLING

It was shown in detail (cf Section C.6) that the easiest way to derive v_2 values for the swollen propellant matrix is to determine the lengths of the swollen and unswollen specimen. Then $v_2 = (\ell_o/\ell_3)^3$. It is, of course important that the matrix releases from the filler particle during the swelling process. This situation is illustrated in Table . The propellant without the bonding agent does not need a pretreatment. Combinations of polar solvent (to swell the bonding agent shell) and non-polar solvent (to swell the HTPB matrix) are to some degree successful. The best method at present appears to be a pretreatment with saturated MEK/H$_2$O followed by

TABLE 93

160°F AGING OF R454 PROPELLANTS NOT CONTAINING THE TEPAN BONDING AGENT

	Uniaxial Tensile Properties at 77°F[a]		
	σ_m, psi	ε_m, %	E_o, psi
	Properties after 8 days ambient cure		
Propellant 1	37	33	147
Propellant 2[b]	40	32	165
	Properties after 16 days ambient cure		
Propellant 1	47	34	176
Propellant 2	49	35	187
	Properties after 27 days ambient cure		
Propellant 1	49	33	168
Propellant 2	48	35	191
	Properties after 2 weeks at 160°F of the propellants cured 27 days at ambient		
Propellant 1	80	26	390
Propellant 2	74	25	350

(a) Standard JANAF Tensile Specimen, $\dot{\varepsilon}$ = 0.74 in./in./min.

(b) Used heat + antioxidant treated R-45M; catalyst was the same in both cases, namely 0.001% $Fe(AA)_3$ + 0.01% HAA.

TABLE 94

EFFECT OF AGING ON L1 HTPB PROPELLANT CONTAINING
88 WT % SOLIDS -- CURATIVE HDI

Propellant	Cure Condition		Aging Condition	Uniaxial Tensile Properties at $77°F$ [a]		
	Time, Days	Temp.°F	Time, Days at 160°F	σ_m, psi	ϵ_m, %	E_o, psi
1 [b]	4	room	-	63	47	270
2 [c]	4	room	-	72	43	300
1	4	135	-	86	41	390
2	4	135	-	136	32	700
1	11	room	-	105	37	410
2	11	room	-	115	36	450
1	11	room	16	123	36	480
2	11	room	16	138	34	560
1	120	room	-	128	35	520
2	120	room	-	145	29	700
1	120	room	30	135	35	550
2	120	room	30	165	27	770
1	11	room	150	164	27	810
2	11	room	150	189	22	960

---

[a] $77°F$, Standard JANNAF tensile specimen, $\dot{\epsilon} = 0.74$ min^{-1}.

[b] Catalyst System: 0.0015% Fe(AA)$_3$, 0.0015% HF$_3$AA.

[c] Catalyst System: 0.0015% Fe(AA)$_3$, 0.0025% HF$_3$AA, 0.1% ZnO.

TABLE 95

EQUILIBRIUM SWELLING OF BONDED[a] AND UNBONDED[b] PROPELLANT
AND PURE BINDER[c] MATRIX OF L1 HTPB

Propellant	MEK/H_2O Pretreatment	Swelling Solvent	Duration of Swelling (Days)	v_2
Bonded	1 day	benzene	2	0.160
	–	benzene	3	0.413
	–	MEK/benzene 1:9	3	0.405
	–	Dioxane/benzene 1:4	3	0.258
	–	DMF/benzene 1:9	3	0.214
Unbonded	1 day	benzene	2	0.176
	–	benzene	3	0.204
	–	MEK/benzene 1:9	2	0.214
	–	Dioxane/benzene 1:4	2	0.226
	–	DMF/benzene 1:9	2	0.232
Unfilled binder	1 day	benzene	2	0.076
	–	benzene	3	0.080
	–	MEK/benzene 1:9	2	0.084
	–	Dioxane/benzene 1:4	2	0.078
	–	DMF/benzene 1:9	2	0.087
	–	MEK	3	0.365
	–	Dioxane	3	0.310
	–	DMF	3	1.0

[a]Propellant contained TEPAN Bonding Agent 88% Solids

[b]No bonding agent present

[c]Binder discussed in Section E4(e)(3)

swelling in benzene, a procedure worked out by C. S. Kim.

Theoretically binder and propellant should swell to the same extent. As Table 95 shows this does not occur and the fault is definitely that of the PBD binder. A polyether propellant, made for comparative purposes showed approximately the same swelling ratio for filled and unfilled binders.

Tables 96 and 97 show swelling data obtained from HTPB propellants shown in Tables 83 and 84 in Section E.4.e.(3) of this report. It is questionable whether this swelling procedure has overcome the restraining effect of the bonding agent shell. The apparent crosslink densities are much higher in the propellants than in the unfilled binder, and it is hard to accept them as valid. The network tightening effect of aging is readily apparent when the data of Tables 96 and 97 are compared. The M values were obtained from Figure 23 using $\mu = 0.40$.

The discrepancy between unfilled binder and propellant swelling ratios would seem to indicate that dynamic measurements on swollen specimens might be more appropriate. Such dynamic measurements on swollen propellants have been repeatedly carried out by a number of workers, and the data were used to calculate the crosslink density according to the well-known formulas of the theory of elasticity or Mooney-Rivlin. These measurements usually consist of determinations of compression modulus or tensile modulus in the swollen state. However, this author knows of no work, where the effect of the solvent pockets, formed around the solid filler, during swelling of composites on mechanical properties has been considered. In a sense a swollen composite may be considered as a foam whose pores are filled with liquid. Mechanically foams differ significantly from the parent rubber. For example the modulus of a foam, containing 50% rubber, is only 1/4 that of the nonporous parent rubber, and similar relations hold apparently for liquid filled foams[13]. Consequently these measurements are apt to indicate a considerably lower crosslink density for the matrix rubber than is actually the case. Presently there is no adequate theory to account for this effect.

in conclusion, it appears that there is presently no satisfactory method available to determine the crosslink density of the matrix of HTPB propellants.

TABLE 96

EQUILIBRIUM SWELLING IN BENZENE[a] OF ROOM TEMPERATURE
CURED HTPB PROPELLANTS

Propellant	v_2	M	$v_e \times 10^4$
No. 1, Table 83	0.149	11,000	0.68
No. 2, Table 83	0.143	12,000	0.63
No. 3, Table 83	0.160	9,300	0.81
No. 4, Table 83	0.153	10,400	0.72
No. 1, Table 84	0.134	14,000	0.54
No. 2, Table 84	0.164	8,800	0.85
No. 3, Table 84	0.156	10,000	0.75
No. 4, Table 84	0.180	7,200	1.04

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[a] After 1 day preswelling in saturated MEK/H_2O.

TABLE 97

EQUILIBRIUM SWELLING IN BENZENE[a] OF HTPB PROPELLANT AFTER AGING 2 WEEKS AT 160°F

Propellant	v_2	M	$v_e \times 10^4$
No. 1, Table 83	0.164	8,800	0.85
No. 2, Table 83	0.160	9,300	0.81
No. 3, Table 83	0.180	7,200	1.04
No. 1, Table 84	0.164	8,800	0.85
No. 2, Table 84	0.184	6,900	1.09
No. 3, Table 84	0.175	7,700	0.98
No. 4, Table 84	0.168	8,400	0.89

After 1 day preswelling in saturated MEK/H_2O.

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13 ABSTRACT

Catalyst systems which strike a satisfactory balance between potlife and time required for full cure have been developed for use in ambient cure catalysis of either R-45M or Li initiated HTPB propellants. The most sophisticated of these consists of the catalyst proper $(Fe(AA)_3)$, a suppressor (HAA and/or α-hydroxy acid) which temporarily inactivates the catalyst, and a scavenger (ZnO) which slowly consumes the suppressor thus reactivating the catalyst. The other systems involve the use of a suppressor, either a chelating agent or an acid, to inhibit catalytic activity (the suppressor subsequently being consumed by reaction with propellant components) or the in situ formation of an active catalyst during cure. Aging, mechanical properties and processing are not adversely affected by these catalyst systems.

It is conclusively shown that the rate of cure will affect the final mechanical properties of the propellant, slower cure propellants being softer.

New information on the complexity of the propellant cure is presented, and new theoretical concepts, which have an important bearing on network analysis and interpretation of experimental data, have been advanced.

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Catalysis of Moisture Reaction						
Homopolymerization of Isocyanates						
Effect of AP on Cure						
Network Analysis						
Analysis of Propellant Matrix by Swelling						
New Catalysts						
Control of Catalytic Activity						
Aging of Ambient Cured HTPB Propellants						